PRACTICAL THERMOGRAVIMETRY

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Abstract

The well-known divergence between the present 'state of the art' of thermogravimetry and industrial requirements is discussed. Sources of errors are analyzed and the optimization of measuring conditions is discussed regarding the problems associated with static and dynamic (flow) atmospheres, and interactions between materials and gases or vapors. Recommendations for gas-flow control systems and vapor sources are given. Thermal stability and the kinetics of gas-evolving, reversible, thermal decompositions of solids are discussed. The scope of TG-derived kinetics for practical use is examined. Some new characteristic points of TG curves are proposed and defined, e.g. 'procedure-independent decomposition temperature' and 'augmented decomposition temperature' (obtained at pseudo-equilibrium conditions).

Keywords: decomposition temperature, error sources, gas-flow and vapor control, kinetics, thermogravimetry

Introduction

Weighing is one of the oldest and the most useful analytical methods [1]. When it became associated with temperature changes, it matured into the recognized method of thermal analysis (TA) called thermogravimetry (TG) [1–3]. The present stage of TG is linked to the availability of sophisticated, commercially manufactured instruments. However, during recent TA conferences (e.g., ICTAC, ESTAC, NATAS) participants are often observed walking past the instrumentation booths while they carry on sophisticated discussions on various aspects of how to better determine the sample's properties, but they do not buy the instruments. Decreasing instrument purchases result, not only from their ever increasing cost, but also from an apparent saturation of the instrumental needs of thermal analysts, which in turn is caused by the decreasing appreciation of TG by industry. At the same time, numerous other researchers in fields outside the sphere of TA, study problems where mass changes are of particular interest, but these are not continuously recorded. Some interactions between materials and gases are studied by very complicated (and costly) methods, without the researchers realizing that continuous recording of mass changes could provide a sur-

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prisingly simpler option and could become a useful method for appropriate monitoring of the progress of the process being tested or developed. This is just a matter of better dissemination of appropriate facts about available TG methods and apparatus.

Examples of such processes, related to either thermal stability, degradation, stoichiometry changes, reaction with gases, synthesis, depositions and/or analytical interactions, include: corrosion, determination of volatile organic compounds (VOC) and outgassing, catalysis, testing of paints and coatings, CVD (chemical vapor deposition), CVI (chemical vapor infiltration), MOCVD (metal-organic vapor phase epitaxy), etching with gases, determination of flammability and smoke generation, coal conversion and liquefaction, removal of sulfur oxides from industrial gases, sorption and permeation of solvent vapors or moisture in plastics, oxidation and reduction processes, making of sesquioxides (superconductors, magnetics), pharmaceutical issues such as water sorption and drying, determination of volatility and vapor pressure, industrial thermal decomposition and drying, 'hot-wet' degradation of materials caused by humidity, material tailoring via high-temperature, high-pressure solid–gas reactions (oxide and non-oxide refractories, inorganic/organic composites, solid state electrolytes), monitoring nuclear wastes, contamination and remediation of soil, controlled interactions with gases to analyze the composition (cements) or monitoring physiological processes (carbon dioxide in photosynthesis or dissolution reactions of biologic and/or bioactive inorganic materials in body liquids). Each of these research/industrial areas involves mass changes, so one can quickly and directly benefit if these changes are continuously recorded, as opposed to the presently common 'before and after' approach.

Incorrectly, thermogravimetry is thought to be limited to very small samples. This perception somehow turns many industrial researchers away from TG. They may also unjustifiably assume that TG's cannot handle corrosive gases, condensable vapors, contaminating fumes, high vacuum or high pressure, or that the durability of specialized TG instruments is limited. These problems have already been solved and in this paper we try to show and explain some of the solutions.

A separate, but general, problem is the tendency of TG instruments to become over-sophisticated, in the form of 'black boxes' (or 'gray boxes') that are easy to operate and provide pre-analyzed results and nicely smoothed data. Computers equipped with powerful programs allow analysis and solution of problems, but it is also easy to pass to the computer the entire responsibility for interpretation of results. If a user accepts a calculated value without taking notice of the error analysis, or without calibration of the entire instrument, (as opposed to calibration of the balance alone), or does not want to learn what physico-chemical processes have really been measured, it is not the computer's fault. In this respect, progress in thermoanalytical instrumentation is apparently proceeding in two opposite directions: towards 'Push-Button' instruments with more and more functions being delegated to the computer and, in the opposite direction, towards more 'transparent' (flexible and easy to observe their functions) instruments, that still require the researcher's involvement and know-how. While the first type have their place in routine analysis, 'transparent'
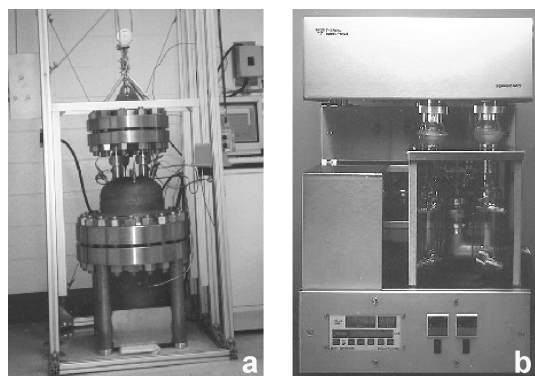
Fig. 1 Examples of commercially available TG instruments, of 'transparent' features;
(photos by courtesy of Thermal Interactions Co.): a – high-pressure TG-DTA;
b – TG system with vacuum and vapor control

instruments should become more appreciated in scientific and industrial research. Examples of some 'flexible' TG systems are shown in Fig. 1.

The 'know-how' issues necessary for successful experimentation and the subsequent interpretation of results will be discussed from two points of view: a) technological (lowest procedural temperature, highest yield and shortest reaction time), and b) scientific (description of the processes in terms of thermodynamics, kinetics and engineering).

Long experience indicates that many difficult thermoanalytical problems can be alleviated by some simple solutions; some examples follow:

- Good temperature calibration in TG can be achieved by using two geometrically similar crucibles instead of one [4]. One of these crucibles was suspended from the TG balance, while the other (located immediately below the former and exposed to the same temperature programme) was used for measuring the temperature inside the similar sample.
- In order to make the weighing of relatively large samples possible, the (common) horizontal suspension of a balance beam was additionally supported by a vertical ribbon [5].
- The goals of extremely costly and complicated on-line tandem TG-MS or TG-FTIR, can be achieved far more easily, and often better, by collecting the volatile decomposition products and analyzing them off-line.
- To analyze the effects of diffusion, two opposite-extreme sample holders were employed [6]; one to enhance external (inter-granular) diffusion by packing the powder sample into several-millimeter-long capillaries, and the other to suppress the influence of that kind of diffusion by spreading a thin layer of the sample over a flat, multi-tier sample holder.
- Approaching the very complex problems of decomposition kinetics from the viewpoints of mass transfer and of heat transfer [7], may clarify much of the present confusion in this area.

• Understanding of the effects of convection patterns near TG samples, and of the drag and buoyancy forces in linear and labyrinth paths, can greatly reduce spurious effects and disturbances [8].

The common idea linking these seemingly unrelated issues is practicality, which is the main subject of this paper.

Limitations of performance of a TG instrument

Any kind of measurement has its limitations, and two opposite dangers are associated with the following:

a) Failing to make the effort to tune the performance to the maximum achievable performance and then being unhappy with excessive and unnecessary errors;

b) Demanding more than is possible; e.g., running TG experiments under extreme conditions of many parameters at the same time (such as temperature, temperature ramping rate, load, gas-flow), and plotting/recording the obtained residual deviations as full scale of the plot without realizing that their magnitude is close to the ultimate resolution of the balance.

There is some confusion about the performance of thermobalances: what the manufacturers claim, is not always the same as what the users see. The nature of this discrepancy is three-fold:

a) Some manufacturers base their claimed performance on results obtained under ideal conditions – often for 'easy' samples, or with no sample at all.

b) The claimed parameters are often those measured separately, or exclusively (e.g., separate performance of the balance, furnace or control-levels and sensors), while the users need them to be inclusive (the practical overall performance).

c) The maximum performance of any instrument obviously cannot be achieved in the worst possible conditions. It should be the user's responsibility to refine the experimental conditions, and if the user is not interested in that, disappointment is inevitable.

Sources of errors in thermogravimetry; optimization of conditions for TG measurements

Modern TG instruments are capable of producing astonishingly precise data (e.g. some of them can record µg mass changes of large samples, weighing up to 100 g). At the same time, if less-than optimum conditions are applied, the balance readings can be heavily distorted, because balances do not distinguish between the forces of interest and disturbing forces. The full extent of the balance performance is achievable and spurious phenomena can be controlled, provided that they are understood.

The most common sources of TG disturbances and errors in the sequence of the frequency of their occurrence [7–10] are:

1. Unstable buoyancy forces;
2. Convection forces;
3. Electrostatic forces;

4. Condensation of volatile products on sample suspension;
5. Thermal expansion of the balance beam (a severe problem in horizontal TG's).
6. Turbulent drag forces from gas-flow.

Note that the first item is the static buoyancy (related to the gas-density), and the last one is the influence of dynamic forces of flow and of thermal convection. It is a common mistake to use the term 'buoyancy' when meaning drag. Both drag and buoyancy depend on the size and the shape of the pan plus sample, on their distance from the baffle tube, as well as on the velocity and the density of the gas. Any instability of those factors will cause erroneous mass readings. The most critical factor in TG experiments is gas handling and this is discussed below.

The question: 'To flow or not to flow?'

TG experiments often require a controlled environment around the sample. Operating the instrument filled with static gas would be expected to be better for the stability of the balance readings than maintaining a gas-flow, but the reality is the opposite. A TG run with no forced gas-flow produces an uneven and irreproducible temperature build-up in the system, resulting in irreproducible mass baseline deviations. In most instruments, it is almost impossible to have a static gas during a TG experiment. Systems containing any gas other than air must be tightly sealed or air will diffuse into the system. If the system is sealed, the pressure will build up and an unstable pressure will result. In both cases the mass readings will drift due to the buoyancy changes which result from heating.

Factors other than buoyancy also make flow beneficial for TG. gas-flowing downwards helps keep the furnace heat away from the balance mechanism. Although some TG balance mechanisms are protected against corrosion, exposure to corrosive gases should be restricted to the reaction zone (hang-down tube). Thermal decomposition often produces volatile and condensable matter, which settles on everything in its path. Whether the balance mechanism is corrosion resistant or not, there can be no protection against contamination – if the contaminants reach the balance mechanism.

Some TG instruments can be used to study very large samples of plastics, rubber, coal etc., without any contamination of the moving parts of the system. These instruments require a constant flow of carrier gas. So a flow of gas, both through the balance chamber and through the reactor tube, prevents the temperature and pressure building up and the baseline is stable. Flow also protects against corrosion and contamination. So if 'to flow – or not to flow?' is the question, then the answer is clear: to flow.

Another general recommendation is to ensure there is no gradual change in the composition of the gases inside of the TG system (both locally and generally) due to incomplete replacement of the previous gas with the new one when the gases are switched. The balance chamber takes longest to switch gases completely. It may be possible with some TG models to evacuate the previous gas from the system and fill it with the new gas. Obstruction of the outlet, changing of the flow rates or the gas pressure, and shutting the purge gas off, even for a short while, can result in an unnoticed

surge of the reactor gas into the balance chamber. The start of a run may have to be postponed until the intruding gas has had time to escape.

The are some golden rules of gas handling in TG:

a) Establish (experimentally) the optimum flows of the gases before the run.

b) Do not change the settings during the entire series of tests; if gases are switched or mixed, the total flow-rate should be kept constant. In this view, the capability of changing the flow rate (not switching of gases) by computer, would be a feature of little practical value.

Patterns of gas-flow in TG instruments with vertical furnaces; how to minimize the disturbances

TG instruments are able to operate with samples exposed to ammonia, water vapor, solvent vapors, HCl, SO_2, fumes and smoke of burning rubber or plastics, coal, etc. In most of these extreme environments, the balance chamber is isolated from the reaction chamber by purging and/or by the procedure known as 'gas-flow separation'. An additional and severe problem is encountered in TG studies in vapors of liquids. Unless proper techniques are used, the data may become erroneous. Attack by aggressive environments, condensation and contamination, as well as unstable buoyancy forces, are best addressed by two kinds of flow pattern:

a) Downward, concurrent flow of the gas which purges the balance chamber ('purge gas') and the reaction gas;

b) Counter-directional flow ('gas-flow separation') of the purge gas and the reaction gas.

The first flow pattern can be generally recommended, due to its simplicity and effectiveness, whereas the latter is invaluable in those difficult cases, where no purge gas can be allowed in the environment of the sample.

Gas-flow separation is possible only if: (a) the purge gas used is much lighter than the reaction gas (helium is the gas of choice); (b) both gases are flowing continuously; and (c) a suitable type of baffling is used.

The use of TG instruments in investigations of interactions between materials and gases or vapors

Traditionally thermobalances have been used mainly to study thermal decompositions of substances and materials; broadly speaking, in 'materials characterization'. However, more and more research is being done in the field of controlled chemical reactions (including synthesis) at elevated temperatures, explored gravimetrically. The sphere of increasing importance of vapor thermogravimetry includes not only the traditional sorption research, but now also the study of equilibria by conducting TG measurements at controlled partial vapor pressures. The desired partial pressure can be achieved either by controlled vacuum, or by dilution of the vapor with an inert gas (cf. Fig. 1).

In a static gas environment, e.g., a TG system first evacuated then filled with the vapor to the desired pressure, the following spurious sources of mass changes may be experienced: (a) sorption of the vapors on the moving parts of the balance mechanism; (b) exposing the moving parts to an environment of non-uniformly distributed density; (c) unstable buoyancy forces.

The resistance of the balance to vapors must be distinguished from the accuracy of the weighing. With improper procedures, the accuracy can be strongly impaired by the presence of vapors. With proper procedures, the balance is as stable as it is when using inert gases. Even if the vapors or the liquids do not damage the balance, any condensation on the moving parts will still ruin the accuracy. The vapors of most liquids do not behave like ideal gases, so, even if condensation of the liquid on the moving parts is prevented, the instability of the density of the environment inside the balance chamber, caused by the changing degree of the aggregation (clustering) of the molecules, makes accurate mass recording impossible.

A TG instrument cannot be casually used with condensable gases or vapors to give a ppm precision. Experience conflicts with the popular preference for the static mode of handling vapors in TG; in contrary, the dynamic mode (when used properly) proves effective, and easier than commonly expected. Figure 2 shows two types of such dynamic vapor generators.
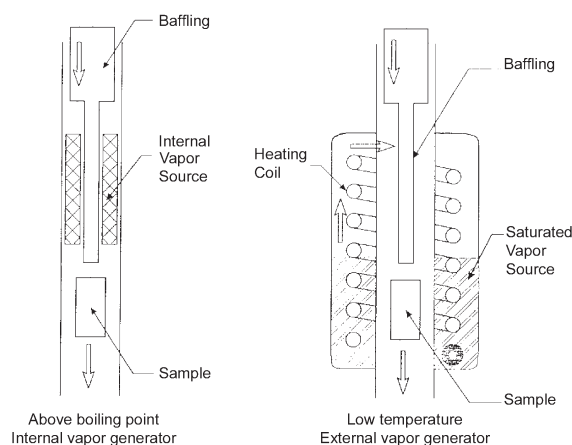

Fig. 2 Two types of vapor generators suitable for TG applications

Requirements and recommendations for a gas-flow control system

A three-gas system normally covers the needs of the vast majority of applications. Stable, non-fluctuating flow (available from electronic mass-flow controllers, combined with high-quality two-stage regulators) is important for stable, repeatable results. Low pressure of the incoming gas (e.g. 0.3 bar) prevents surges of gas when the solenoid valve opens. This is important if gas is to be introduced into a system after a

previous evacuation. Additional needle valves can be recommended. Note: gases which are kept in cylinders in liquified form, e.g. sulfur dioxide, maintain almost constant pressure; unlike nitrogen, helium, compressed air etc., where the pressure in the cylinder decreases with consumption. When sulfur dioxide leaves the cylinder, it does so at the expense of the liquid phase, so the pressure varies only if the liquid's temperature does. Thus no cylinder pressure regulator may be necessary at all, as long as the pressure does not exceed the rated value of any of the components used. For mass-flow controllers, the maximum allowable differential pressure is usually at least 3.5 bar, whereas the pressure in a cylinder of sulfur dioxide is 2.3 bar at 21°C, so an expensive corrosion-resistant cylinder regulator is not necessary in this case (this has to be checked however with the safety officer).

The internal volume of the lines between the flow-controllers and the thermobalance should be kept to the necessary minimum. Two or three fluctuation-free flow controllers, capable of maintaining a stable flow in the range 20 to 200 mL min^{-1} (for the minor component of a gas mixture, the 0 to 20 mL min^{-1} range may be better) and of returning to the same pre-set value with a precision of ±1%, would be ideal. Electronic mass-flow controllers are preferable and they make it easy to handle the gas-flow. If cost is the limiting factor, needle valves combined with flow meters can be used instead, but there is not a substantial saving.

Rotameters are less satisfactory than mass-flow controllers because they require adjustment if the delivery pressure changes and it is very difficult to return to the previous settings precisely – an easy job for digital mass-flow controllers.

All the materials used in the system must be compatible with the gases used. Teflon, Viton, Kalrez and similar materials should be specified when ordering controllers intended for aggressive gases and vapors. For ultra-pure gases, only all-metal lines, filters and regulators should be used (general-purpose regulators have a rubber membrane, so ambient air does diffuse into it).

Unobstructed flow in the vent should be maintained while gas is being let into the thermobalance. Any bubblers or liquid-filled scrubbers connected downstream from the TG should be avoided in order to maintain a stable base-line. This obviously does not apply if any hazardous gases are involved. Exhausting of the gases should be safe and in compliance with the regulations pertaining. Fine gas-filters located upstream from the flow controllers are recommended. Check valves (completely leak-tight models) should be used (with proper polarity) to prevent back-streaming of gases in all cases where cylinder pressure regulators are not used, and/or when the gas lines are inter-connected. It is important to remember that a thermobalance itself is always such an inter-connection.

Thermal stability and the dynamics of gas-evolving, reversible, thermal decompositions of solids

The present state

Kinetic analysis of macro-scale heterogeneous processes is one of the most complex tasks of solid-state chemistry [7, 11], well demonstrated in the early studies on decomposition of real pieces of limestone [12]. There are many alarming discrepancies between laboratory results and industrial-scale problems. So-called thermoanalytical kinetics has been studied for several decades and there are now a thousand or more papers describing numerous methods for determination of kinetic parameters. Most of these methods result from a combination of various well-defined geometrical models of the idealized advance of a reactant/product interface with the generally accepted exponential Arrhenius equation [13]. Problems that are often ignored include: (a) Do chemical kinetics really apply in the given case, particularly when transport phenomena [10] such as macro-diffusion of gas from the reaction interface or from the crucible; or flow of gas through the gaseous envelope, or heat transfers, are prevailing? (b) Do strictly 1-, 2- or 3-dimensional models truly match with the actual sample microscopic morphology? Microscopic observations seldom comply with such simple geometry. There is often non-uniformity, distortion, strain or intergrowth of reactant particles [14]). (c) If the process is truly controlled by micro-solid state kinetics, the three basic categories of models [15], (i.e., diffusion, nucleation-and-growth or boundary motion) can only be distinguished, producing inseparable TG curves of each category. (d) Do the calculated kinetic parameters (usually labelled as 'activation energy' and 'frequency factor') have any physico-chemical significance, or are they just procedural (and often meaningless) numbers [10, 13]? (e) A third kinetic parameter which is sometimes reported instead of the reaction model, is the apparent 'reaction order'. Do these values have a physico-chemical interpretation when applying a formal kinetic equation, or do they express a fractal (non-integral) geometry [16] of the sample morphology?

None of the reported kinetic methods produces satisfactory results when applied to the apparently simple case of a reversible thermal decomposition of the type [7, 12, 17, 18]:

$$A_{solid} \rightleftharpoons B_{solid} + C_{gas}$$

for example, the repeatedly discussed decomposition of $CaCO_3$, with its countless values of experimentally determined activation energies. Because of these drawbacks, thermoanalytical kinetics is generally not employed in practical engineering studies. A few engineering researchers use the literature models of their preference [13], or simply use the algorithms they have purchased with their instruments, with often misleading and ungrounded claims, and yet another publication is the only benefit.

The discrepancies and inconsistencies reported in the literature are sometimes large. Some calculated values are obviously nonsensical, e.g., negative activation energies, and there is often virtually no correlation of the values obtained from thermal

analysis experiments with those typical for larger-scale industrial processes. Therefore the chances of practical utilization of the kinetic data to predict real-life processes are greatly decreased. To minimize diffusion effects, established kinetic practice requires that samples for study should be as small as possible (thin layers [6]). However, the smaller the sample, the greater is the ratio of its surface to its bulk and this may overemphasize surface reactions and make correlation with large-scale processes poorer. Experience shows, however, that even very small samples (less than 1 mg) are far from being small enough to be free of diffusion inhibition. To justify the obvious errors, the adjectives: 'apparent', 'formal' and 'procedural' are used in conjunction with the otherwise strictly-defined terms of 'activation energy' and 'reaction order' as known in homogeneous chemical kinetics.

The value of the activation energy calculated for a reversible decomposition of a solid may, thus, be just a procedural value of no real physical meaning other than a number characterizing the individual thermoanalytical experiment (Garn [19, 20] pointed this out some 40 years ago). There are a few critics who say that, if the assumptions for a theory are not fulfilled, the results cannot be correct [21]. They, therefore, insist that the Arrhenius equation, which was originally empirical, but was later theoretically justified in terms of a model derived for collisions of molecules in homogeneous systems, cannot be applied to non-homogeneous reactions in its original sense. A comprehensive synthesis and elucidation of this complex and confusing problem was recently given by Brown [22].

Many sophisticated kinetic methods neglect the distinction between micro-kinetics (molecular level, true chemical kinetics) and macro-kinetics (overall processes in the whole sample). The above-mentioned process of $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$, as applied to the whole sample, consists of many elementary processes, some of them of purely physical in nature (e.g. heat transfer, diffusion). Experimentally obtained kinetic data can refer to only one of them – the slowest one. If that step is of physical, sample-related nature, no chemical-kinetic information can be derived from such a TG curve. Undoubtedly, there are many other kinds of TG processes that are controlled by chemical kinetics, e.g. thermal decomposition of some polymers; here we discuss gas-producing reversible thermal decomposition. Rather than assuming that a TG curve reflects the chemical kinetics, we propose to examine in each case whether that kinetics is of chemical or of physical nature. The next chapter discusses ways of achieving that.

Macro-kinetics by thermogravimetry

The temperature dependencies of heat and mass transfers can differ from those derived for purely chemically-controlled reactions. It can be mentioned that the approximately linear Newton's law can contrast with the exponentially reliant Loeb or Lonius equations, etc. [13]. If, in the first approximation, the actual temperature dependence is known, the value of the logarithm of this dependence can presumably indicate what the limiting step may be. If the logarithm is around unity, the limiting step could be related to heat transfer, while if the logarithm falls within 1.5 to 2, a diffu-

sion controlled process is more likely, and if the logarithm attains any significantly higher values, chemical control (following the traditional Arrhenius equation) may be indicated. The currently accepted thermoanalytical kinetic processing [13, 21] will be adequate only in this last case.

The decomposition rate of the same sample, in the same vessel, but at various values of the isothermal temperature should preferably be recorded. If the process is diffusion-controlled, this can be confirmed by measuring the magnitude of the influence of diffusion-related factors, e.g., the size and shape of the sample, or by varying the partial pressure of the volatile decomposition product, up and down from the basic conditions of the experiment. The magnitude of the resulting variation in the reaction rate is then compared to the magnitude of the change calculated for a diffusion-controlled process. If, for example, the decomposition of a hydrate is studied in an environment of 10 mbar of water vapor, the run should be repeated twice: say under 9 mbar and under 11 mbar (such instruments are now commercially available). If the magnitude of the change in the reaction rate by diffusion-related factors is negligible, but the temperature dependence is strong, the process may follow the Arrhenius equation and kinetic equations based on it. If the magnitude of the measured temperature-related changes in the reaction rate is in the range typical of diffusion-controlled processes, the process probably is diffusion-controlled. A simplified way of determining whether a given reaction is mass-transport controlled, would be to compare (in a non-quantitative way) the TG curves obtained when the degree of the hindrance of removal of the volatile products of the decomposition is changed. This could be done using the same sample and sample holder, but by covering the container with a lid. Alternatively, labyrinth-type crucibles known in derivatography can be used, or powder samples can be packed into capillaries [6]. Such relatively minor changes should not significantly affect the rate of bond-breaking steps. Heat exchange may be affected more, but that is likely to be a negligible factor.

Whether or not the process is controlled by heat transfer (hence this applies only to programmed temperature experiments, or the initial stage of heating to the isothermal temperature), that can be tested by slight increase in the ramping rate. If heat transfer is the controlling process, the rate of the mass loss will not increase, or the approximately straight segment of the TG curve (plateau on the DTG curve) will become straighter and longer. The temperature range of the decomposition process will not shift towards higher temperatures. The magnitudes of the influences of temperature-related factors, e.g., changing the thickness of the walls of a highly-conductive sample holder; adding or removing thermal insulation; comparing the decomposition in shiny and in black sample holders, or by making the temperature oscillate (square wave) very slightly around the set isothermal level, can all be investigated. Where heat flow is rate controlling, the response should be directly proportional to the magnitude of the temperature jumps.

If it turns out that the process is controlled by chemical kinetics, the resources of classical thermoanalytical kinetics [13, 21] can be used.

Scope of TG kinetics in practical use

Processes involved in thermal decomposition

Kinetics deals with time-related calculations. Engineering applications require: (a) determination of the optimum temperature region (from the economic viewpoint) for carrying out the industrial process; (b) prediction of the yield after a specific time of a thermal process; (c) estimation of the time necessary to achieve a specific yield; (d) determination of the characteristic parameters (whatever one wishes to call them: 'order/orders of the reaction', 'activation energy' and 'pre-exponential factor') and any dependence of their values on the extent of the process; (e) definition of the character of the process mechanism (macro/micro, nature of the rate controlling process); (f) comparison of modified plots of empirical data, with theoretically-derived plots in attempts to verify or better elucidate the process mechanism.

A point of major controversy in kinetic analysis is the problem of the kinetic compensation effect [13] (which involves the mathematical correlation of A and E). The Arrhenius equation in its standard exponential form is: $k=A\exp(-E/RT)$ where the symbols have their traditional meanings of reaction rate constant, pre-exponential factor, activation energy, gas-constant and temperature. To shed some light on the complexity of the procedural effects, the critical processes involved are listed and divided into two classes in Table 1.

Table 1 Distinction between the micro- and macro-kinetics of reversible thermal decomposition of solids

Micro-kinetics: molecular level intra-crystal processes	**Macro-kinetics:** sample level intra-container processes
Decomposition is influenced by the following factors that are internal to the process: • mobility of crystal lattice, affecting transfer of heat (the equivalent of molecular collisions, that the Arrhenius equation was derived for); • enthalpy of decomposition; • activation energy of decomposition of molecules; • crystal size and defects, affecting the surface energy (different from the bulk energy and the lattice mobility); • structural differences between the reactant A and the solid product B; • nucleation and growth of B; • decomposition temperature (its thermodynamic value)	Decomposition is influenced by the following factors that are external to the process: • concentration of the gaseous product C in the immediate vicinity of the B-to-C interface; • inter-granular diffusion; • pressure, composition and flow of gas between the grains; • catalytic capabilities, interface curvature, capillary effects; • shape of sample holder; • external gaseous envelope; • granulation and porosity; • thermal conductivity of the (porous) sample, and of the sample-holder's walls; • heating rate in case of non-isothermal experiments; • procedural decomposition temperature, varying largely as a function of the partial pressure of C

Obviously, in thermal analysis it is the macro-kinetics that is recorded. Chemical-type, or micro-kinetics, where the Arrhenius equation applies, usually governs only one of the steps of the thermal decomposition of a sample as a whole. Whether this step has a controlling role has to be determined, not just assumed, in each experiment. The thermoanalytical literature is full of examples of diffusion (on the sample level) being the rate controlling process. There is no question that micro-kinetic processes do take place, therefore the required complexity of a theoretical model capable of describing all the steps involved would be enormous. Fortunately, no matter how many elementary processes are occurring concurrently, at a given moment usually only one of them (the slowest one) is determining the actual (measured) reaction rate.

Sometimes a formal description based on two parametric 'orders' seems to satisfy the fractal geometry of a particle's topology [14, 16], because classical reaction kinetics [13] has been found unsatisfactory when the reactants are spatially constrained on the microscopic level by either walls, interfaces, faults/dislocations or force fields [14]. This is caused by the effective dimensions resulting from relations between mathematical sets and natural objects (the world of fractals [16]), where microscopically observed structures are impossible to characterize by a simple geometry, similarly to our inability to describe precisely a cloud or a tree. Commonly, nucleation/diffusion controlled reactions [13] are conveniently described on the basis of exact topological dimensions, using one-, two- and/or three- dimensional objects. This seldom enables correct modeling if the naturally occurring shapes exhibit non-isotropy, non-sphericity, polydispersity and overlapping as is often seen even by standard visual observations. This problem is frequently overcome by the introduction of stereology and similarity laws [14] in order to match the non-integral reaction orders that often result from practical evaluations [13]. Coexistence of fractal and topological dimensions is a matter requiring bridging of traditional dimensionality and fractal geometry to open up a new area of kinetics.

In a reversible, gas-evolving reaction, the term 'temperature of decomposition' is not well-defined. For a reaction with no gas evolution, the thermodynamic decomposition temperature would be the temperature below which the reactant is energetically stable and above which the product is stable. However, for the type of decomposition discussed above, the equilibrium temperature depends on the partial pressure of the gas, C, i.e., the so called equilibrium background [13] of a variant reaction is pressure-dependent, similarly to the conventional temperature-dependence [13].

Is decomposition related to evaporation?

A gas-evolving, reversible thermal decomposition resembles the process of removing vapor from the surface of its liquid. From the viewpoint of the mass loss rate, both thermal decomposition (the kind discussed) and evaporation of liquids (e.g., from wet sand) behave in the same way. The equilibrium pressure of vapors over a decomposing compound is always lower than the equilibrium pressure of the same vapors over the liquid itself, but this is about the only difference between the decomposition and evaporation.

L'vov *et al.* [23] have recently published a series of interesting papers based on the initial step in the decomposition of a solid being vaporization, followed by condensation of solid products. This suggestion, supported now by considerable evidence, is worthy of attention.

A typical example: decomposition of some hydrates

To illustrate the problems discussed, we refer to some published TG results [24] for the hydrates of copper sulfate and magnesium sulfate, which were obtained over a broad range of conditions of hindrance of escape of water vapor. What causes these hydrates, commonly believed to be stable at room temperature, to decompose rapidly and release their water much below the boiling point of water? Let us visualize the processes involved, and discuss in detail the concept of decomposition temperature.

The observed behavior of the hydrates can be explained if the kinetics of these decompositions are limited by the rate of escape of the gaseous product, C (water). Even at room temperature, the decomposition is fast whenever the volatile product is being rapidly removed. When C is not removed, the decomposition almost stops and the reactant seems (erroneously) to be stable. It would be unreasonable to interpret this behavior in any micro-kinetic terms. This means that the decompositions of these, and many other hydrates which behave similarly, are diffusion-limited (but the controlling factor is effectively the concentration of C).

At a given temperature, either A or B is the energetically stable form, but not both. When the temperature of the substance rises, at the point marked [24] as 'PIDT' (procedure-independent (equilibrium-like) decomposition temperature) the decomposition and the recombination have equal likelihoods. Above the PIDT point, the decomposition into B+C is energetically favored, but the decomposition would be suppressed if molecules of C are present in the immediate vicinity of the surface of A. In that case the equilibrating temperature is increased to a new value; let us call it the 'ADT' for 'augmented (pseudo-equilibrium) decomposition temperature'.

If the pressure of C is constant with time and uniform in the whole sample, and there is no air or other gas in the vessel, the ADT is still a sharp point. If it is not a sharp point, this indicates a coexistence region of mixtures of A and B. Such coexistence means the existence of a reaction front, or possibly enforced metastability, of A beyond its true stability range. Such metastability can occur when the partial pressure, p_c, is not a constant value, that is if p_c varies with time, location, or both. The section of the TG curve associated with the ADT is the temperature range where both A and B forms co-exist in a negative feed-back of a dynamic pseudo-equilibrium (Fig. 3). Labyrinth crucibles, often used in 'derivatography' [25, 26], are useful qualitative tools for providing saturation conditions of the volatile decomposition products, and improving the reproducibility of the data.
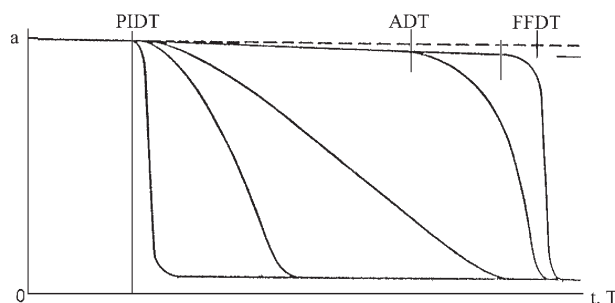
Fig. 3 Graphical representation of thermal decomposition at various constant values of
the gaseous product, being the only component of the environment
Explanation of proposed definitions and their symbols, for TG curves obtained
at various degrees of hindrance of escape of the gaseous product of the decom-
position.
α – conversion ratio (degree of completion of the process);
t, T – time and/or temperature (linear heating); PIDT – procedure independent
decomposition temperature', also referred to as the 'pivoting point'; ADT –
'augmented decomposition temperature' also called 'procedural decomposition
temperature', as classically defined elsewhere. FFDT – 'forced flow
decomposition temperature'. The dashed line is extension of the initial, perfectly
horizontal section of the TG curve

True-horizontal and pseudo-horizontal sections of TG curves

Let us return to the concept of the PIDT point, that separates two sections of a TG
curve: the perfectly horizontal section (if it exists), and the inclined one. It would be
possible to see the PIDT if the TG curve was obtained without diffusion hindrance
(samples usually not larger than 1 mg, under vacuum). Even if these two slopes differ
almost insignificantly, that elusive point remains the borderline between the stability
ranges of the substances A and B. By hindering the escape of gas we can decrease the
slope of the inclined section even to zero, and then the point PIDT would seemingly
disappear. The reason why the distinction between the perfectly horizontal and the in-
clined section of TG curves is important, is as follows. Below the PIDT, curves are
horizontal because decomposition cannot occur due to thermodynamic factors.
Above the PIDT, curves can still be horizontal because decomposition cannot pro-
ceed due to accumulation of the product. Another important difference between the
two sections is that only in the inclined section is the slope diffusion-dependent, be-
cause in the true-horizontal region molecules of the gaseous product C do not form. It
may not be possible to see the PIDT point on a TG curve and only the ADT instead,
but this does not make the ADT the same as the PIDT. Even if the PIDT is hidden, its
value is fixed. Extrapolation of such a TG curve produces the ADT, not the PIDT.

If the escape of gas C is completely free, the ADT will disappear and the true
pseudo-equilibrium PIDT emerges. Such elimination should be ensured and verified,
not just assumed. A suggested procedure, which satisfies such requirements, would
be as follows: (a) place not more than 1 mg of the powdered sample in a TG sample

holder, at ambient pressure and temperature, and record the mass for at least several hours; (b) continue the recording for several more hours while evacuating the TG system; (c) keep evacuating and apply very slow linear heating; (d) the lowest temperature that will start a measurable slope, is the PIDT.

There may be cases when the PIDT cannot be obtained because the substance can decompose under vacuum even at room temperature (so no true horizontal baseline is obtained under vacuum). The PIDT then lies in a lower temperature range than that being considered.

Does a 'decomposition temperature' actually exist? By definition, as long as the reaction is reversible, there is a never-ending competition between decomposition and recombination. At equilibrium, molecules of C are constantly being produced and consumed, but if the liberated C molecules are removed, then we have a non-equilibrium situation and substance A decomposes irreversibly until it disappears completely. These processes take place at any temperature within the reversibility range.

Most such decompositions are endothermic and the entropy of decomposition is also positive [21], so the Gibbs energy change for decomposition will only be negative at high T and positive at low T. ΔG at temperature T will be given by $RT \ln(Q_p/K_p)$ or $RT \ln(p/p_{eq})$, where Q_p is the reaction quotient, p is the actual pressure of C, and p_{eq} is the equilibrium pressure of C at T. When p is kept small, ΔG will be negative at all temperatures T, but the rate of decomposition will be determined by the Arrhenius equation. Therefore in reversible processes there is no unique decomposition temperature. The term 'decomposition temperature' has a thermodynamic meaning of the switching point at which the decomposition reaction replaces the recombination reaction as the thermodynamically favored process (with other conditions such as pressures of any gases held constant). However, TG curves do not reflect thermodynamics, and this is not the matter of approximation. The conclusion is: decomposition temperature cannot be determined from a single TG curve, but it can be determined from a specific family of curves, obtained in the procedure described above in this paragraph.

Discussion of the conventional terms pertaining to decomposition temperature

Not only the physical meaning, but also the earlier metrological definitions of 'decomposition temperature' do not seem to be consistent. The terms 'decomposition temperature', 'procedural decomposition temperature' ('PDT') or 'initial temperature' ('T_i') are often defined as the lowest temperature at which the rate or the cumulative mass change of the decomposition is measurable. The symbol T_1 is also used for that, sometimes marked as '$T_{0.01}$' (for the transformation ratio, α, as low as 0.01).

A 'temperature of thermodynamic stability' (T_{th}) is defined as the 'temperature at which the partial pressure of the gaseous product equals the ambient pressure.' It is

believed that for the decomposition to take place, the temperature must be 'the lowest temperature at which the decomposition is measurable' (T_1, $T_{0.01}$, T_i, PDT).

The physical meaning of lowest temperature at which the rate or the cumulative decomposition is measurable, is inevitably narrowed to the particular conditions and sensitivity of the thermoanalytical experiment. In the first approximation it has no absolute value, in the same way as the beginning of a TG-recorded evaporation of a liquid below its boiling point would be a merely procedural value, lacking any absolute physical meaning. It has also very limited practical significance. The literature abounds in examples of the fact that appreciable decomposition is often recorded at temperatures much below the values generally accepted or expected. For example copper sulfate pentahydrate is capable of producing TG curves, for which the T_1, $T_{0.01}$ or T_i can be sometimes as high as 100 and as low as 40°C. One can justifiably interpret these facts in the following way: copper sulfate pentahydrate decomposes below room temperature, but it appears stable because the decomposition in a closed container at room temperature is hindered. Therefore neither 40 nor 100°C are values of any absolute meaning. If the TG examination of a small sample of that hydrate had started, not at 20°C but below room temperature, the apparent decomposition temperature would be even lower than 40°C.

For very carefully planned TG experiments, 'practically horizontal' curves can be obtained and the PIDT, measured as the 'first detectable deviation', then becomes an absolute value. Relying on the ADT as an indication of the limits of thermal stability of a substance can be a dangerous mistake. The only reliable value representing thermal stability is the PIDT.

Small or large samples?

To minimize the influences of transport processes, established kinetic practice requires that samples for study be as small as possible. Experimental data show however that even very small samples are almost never small enough to eliminate diffusion control. The only conditions that are diffusion-free, are when the sample is spread to a single-crystal layer and exposed to vacuum. Milligram-size samples are not much closer to micro-kinetics than gram-size ones, the reaction remains topochemical even for the smallest samples, and reaction fronts are always created.

A disadvantage of small samples is that they provide very poor correlation with large-scale industrial processes, which by definition are affected by transport of heat and gas. The experimental approach suggested then is to obtain thermoanalytical data in a self-generated atmosphere using relatively large samples and tight containers, and to compare such data with those obtained when the sample is extremely small and the process is completely diffusion-free. The question whether TG samples should be small or large then ceases to exist, because thermogravimetric characterization of a substance should always cover the full range of the limiting parameters from examining sub-milligram samples under vacuum, to large samples in self-generated atmospheres.

Conclusions

The future role of TG instruments is anticipated to become gradually reduced to verification of the validity of highly computerized modeling that would gradually include all the possible processes discussed above. Such an extensive theoretical treatment, that would comprehensively cover all the various aspects of a detailed scientific and engineering description, would become the principal method for the forthcoming prediction of the behavior of materials. It would essentially lower the number of instrumental measurements and save both time and labor. Experimentation would, however, need to be perfected to such an extent that each measurement is reliable and meaningful. Not all measurements are yet adequately reliable. Artifacts are easily produced if we allow a computer to plan an experiment for us. This is frequently the case when 'rate-controlled TG' is used. Many thermal processes are characterized by TG curves consisting of more than one mass loss step. This may result from a sample being a mixture, or from the reactant undergoing a multi-step thermal transformation. These TG steps may overlap partly or completely. When the stoichiometry of a multi-step TG process is determined, the mass value at the horizontal section of the TG curve is used as the indicator of the stoichiometry. This is the basis for 'compositional analysis'. If no horizontal section between the steps exists, the inflection point is used for that purpose. The inflection point on a TG curve can be precisely determined from the DTG curve, but the inflection point is not a direct indication of the stoichiometry in the common situation of incompletely separated TG steps. The mathematical addition of partly-overlapping individual TG steps (or of any other curves of similar shape) produces TG curves whose inflection points consistently fall below the stoichiometric values. This fact (belonging to analytical geometry) is seldom realized in thermal analysis. It is frequently observed that the location of the inflection point varies for TG curves obtained under different conditions. These shifts are attributed to experimental parameters, such as sample geometry. In the case of partly-overlapping TG steps, the common practice of using the inflection points to obtain stoichiometric values, may lead to systematic errors of up to 20%. Moreover, the common practice of attributing those 'shifts in the stoichiometric values' to changes in the reaction mechanism seems to be disputable, unless supported by other facts. A practical way of finding the inflection point is to use an appropriate deconvolution program on the DTG curve.

The largest errors can result when the single steps that make a combined two-step TG curve are symmetrical. Asymmetrical steps produce smaller errors, because the mass changes are much slower at the beginning of the second step, than at the end of the first one. Therefore the error caused by including the initial mass changes of the second step into those of the first step are less significant.

For two decades, attention has been focused on milligram-size samples. Now there is a growing recognition of the fact that larger (mass and/or volume), more representative samples, are very important for studying inhomogeneous materials such as coal, plastics, rubber, composites, surface-coated parts or soil samples, as well as (basically) homogeneous industrial raw materials such as carbonates or hydrates. If

we can provide kinetic models that can be reliably extrapolated to industrial conditions, the trust of industry in thermal analysis can be restored. Such new kinetic models may be based on the macro-kinetic interpretation proposed in this paper.

Despite the expected overwhelming role of computers in the future, we are sure that scientific 'sense, instinct and intellect', together with traditional 'know-how', will survive in the technical growth anticipated in the third millennium. There will still be space for devoted scientists to enjoy the sophistication of science to where, undoubtedly, the art of thermogravimetry belongs.

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