Thermogravimetric Analysis

A Review*

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THERMAL methods of investigation, generally referred to as thermo- or thermal analysis or thermo-analytical techniques, have found wide application in recent years.[1]   These may be defined as experimental methods for characterising a system (element, compound or mixture) by measuring changes in physico-chemical properties at elevated temperatures as a function of increasing temperature.[2]   The two chief methods are (*a*) differential thermal analysis,[3] in which changes in "heat content" are measured as a function of increasing temperature and (*b*) thermogravimetric analysis, in which changes in weight are measured as a function of increasing temperature.   Other methods that come within this definition involve the use of changes in gas volume or pressure; changes in solid volume; changes in electrical resistance; changes in ultraviolet, visible or infrared transmission or reflectance.[4]

The two techniques, (*a*) and (*b*), provide information relating to certain physical and chemical phenomena, which are listed below—

Physical Phenomena	Chemical Phenomena
Crystalline transition	Chemisorption
Second-order transition	Desolvation (especially dehydration)
Fusion	Decomposition
Vaporisation	Oxidative degradation
Sublimation	
Absorption	
Adsorption	Solid-state reactions
Desorption	Solid - gas reactions (*e.g.*, oxidation or reduction)

The basic instrumental requirements for thermogravimetric analysis are a precision balance and a furnace that is programmed for a linear rise of temperature with time.   Thermogravimetry can provide information on all the phenomena listed above, except crystalline transitions, fusions and those solid-state reactions that occur without change in weight.

Although information can be obtained by carrying out the weighing operations manually, nowadays automatic continuous recording of the weight and temperature are usual; the continuous record of weight and temperature ensures that no features of the weight loss - temperature curve are overlooked.   The results from a thermogravimetric run may be presented by—

    (*i*) weight (corrected weight—see below on "Corrections", p. 908), *versus* temperature (or time) curve, referred to as the thermogravimetric curve, see Fig. 1 (*a*), or

    (*ii*) Rate of loss of weight *versus* temperature curve, referred to as the differential thermogravimetric curve, see Fig. 1 (*b*).

In (*i*), the weight axis may be scaled in one of several ways, *e.g.*, (*a*) as a true weight scale, (*b*) as a percentage of the total weight, (*c*) as a percentage of the total weight loss or as a fraction

* Reprints of this paper will be available shortly.   For details, please see p. **984**.

of the total weight lost, (d) in terms of molecular-weight units, or (e) expressed in terms of α (where α = fraction decomposed). (When the molecular weight of the compound is known, method (d) affords a convenient method of plotting the results, since it is easy to extract data relating to lost fragments, for example, in the study of an inorganic complex—it also forms an easy method of comparison of a family of such compounds.) The use of method (e) should be limited to a single-stage process, i.e., a special instance of (c).

The following features of the thermogravimetric curve may be identified—

(i) A horizontal portion or plateau, which is indicative of constant weight.

(ii) A curved portion; the steepness of the curve is indicative of the rate of weight loss, and this will obviously pass through a maximum, giving an inflection with $\frac{dw}{dt}$ as a maximum. The shape of the curve is dependent on the variables discussed in the section on "Techniques" (vide infra).

(iii) An inflection (at which $\frac{dw}{dt}$ is a minimum, but not zero) may imply the formation of an intermediate compound. It may, however, be due to disturbances in the heating rate or in thermocouple response. It is necessary to ensure a regular rise of temperature,[5] and therefore it is desirable to have an independent temperature - time record to ensure the reliability of the results.[6]

The portion of the differential thermogravimetric curve lying on the line $\frac{dw}{dt} = 0$, see Fig. 1 (b), is equivalent to the horizontal portion of the thermogravimetric curve. The peak of the differential thermogravimetric curve corresponds to the curved portion of the thermo-
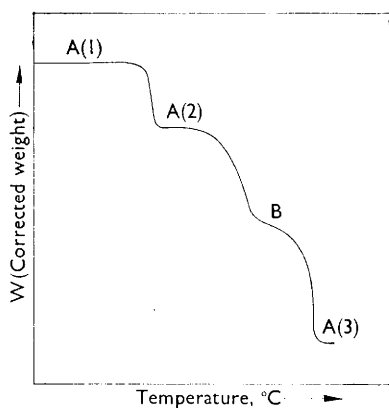

Fig. 1(a). Thermogravimetric curve: A (1), (2) and (3) are plateaux in the decomposition curve of the material. B is a point of reflexion (at which $\frac{dw}{dt}$ is a minimum)
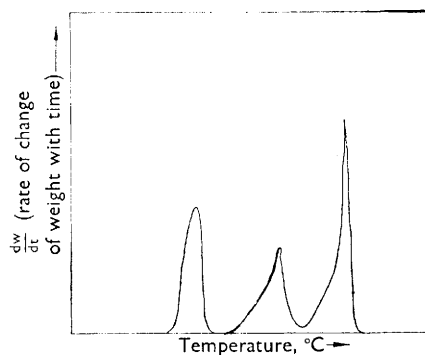
Fig. 1(b). Differential thermogravimetric curve: A (1), (2) and (3) correspond to the plateaux on the thermogravimetric curve (at which $\frac{dw}{dt}$ is zero). Trough B corresponds to the point of inflexion on the thermogravimetric curve (at which $\frac{dw}{dt}$ is a minimum)

gravimetric curve, whereas the peak maximum of the former is identical with the point of maximum slope of the latter. A trough on the differential thermogravimetric curve corresponds to an inflection at which $\frac{dw}{dt}$ is a minimum on the thermogravimetric curve. The height of the trough above the line $\frac{dw}{dt} = 0$ affords some measure of the stability of the intermediate and the extent to which the two consecutive reactions (corresponding to the peaks on either side of the trough) overlap. The differential thermogravimetric curve offers certain advantages over the thermogravimetric curve in the matter of presentation. Features in the thermogravimetric curve that are not readily discerned are more clearly seen in the differential thermogravimetric curve, e.g., any change in the rate of weight loss may be seen immediately

as a trough, indicating two consecutive reactions, or as a shoulder to the peak, indicating two almost overlapping reactions or as a tail to a peak, which is probably an indication of strong adsorption of the volatile product on the new solid phase.[7] Differential thermogravimetric curves often show considerable similarity to differential thermal analysis curves or permit a ready comparison to be made.[8,9,10]

The use of thermogravimetric results for evaluating thermal stability has focused attention on finding a workable definition for a suitable standard for describing decomposition. The temperature at which a reaction begins in any particular thermobalance run is dependent on many variables, of which the rate of heating is perhaps the most important. This temperature is neither a true decomposition temperature, below which the reaction rate is zero, nor is it a transition temperature.[11] In fact, there is often little correlation between results from isothermal runs and non-isothermal runs.[5] Newkirk[12] argues that knowledge of this temperature is useful and the term "procedural decomposition temperature" used by Doyle,[13] in his polymer studies, stresses the dependance of this temperature on the powerfully influential procedural details. Pellon[14] in his work on the stability of phosphorus-containing polymers uses a temperature T_{10} (a temperature at which the cumulative weight change reaches 10 per cent.) as a means of defining thermal stability. A comparison of decomposition temperatures has often led to controversy owing to a lack of appreciation that the value is a function of method, apparatus and procedure. A clear statement of conditions used should be stated when quoting decomposition temperatures. Guiochon[11] comments: "Thermogravimetric measurements are easy to carry out, but somewhat difficult to account for."

A survey of the history of thermogravimetric analysis up to 1940 has recently been published by Duval,[15] in which he traces the design and construction of the first thermobalance back to Nernst and Riesenfeld[16]; Wache[17] has written an article on Chevenard. The second edition of Duval's book, which is now available,[18] is divided into a discussion of (*a*) "The Thermobalance" and (*b*) "The Thermolysed Substances." Review articles have been published on recording balances and instrumentation[19,20] and on thermogravimetry.[21 to 27] Several symposia have been held, notably in the United States.[28,29] The inception of the first Thermoanalysis Institute held at the Fairleigh-Dickinson University, New Jersey,[30] occurred in 1962. A survey of literature, published about four times a year, commenced in May, 1962.[1]

TECHNIQUES

This section is concerned with two aspects of thermogravimetry. The first arises from the dynamic nature of the method, and the second is concerned with the factors influencing the shape of the thermogravimetric curve, and these must be taken into account to obtain meaningful and reproducible results, so that thermogravimetric data on different compounds can confidently be compared.

CORRECTIONS—

If a crucible, that is known not to change weight, is heated when empty, there is, generally, an apparent change in weight with increasing temperature (see Fig. 2), *e.g.*, a
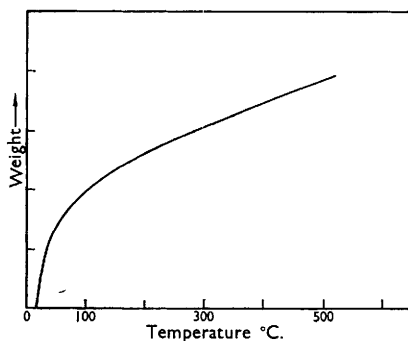

Fig. 2. Typical correction curve

crucible weighing 2 g would be expected to have an apparent change in weight at $1000°$ C of, say, 0·1 per cent. of the crucible weight; this would amount to an apparent change in weight of 2 per cent. if the sample weighed 0·1 g.   This apparent weight change is caused by the interplay of a complex combination of several factors, such as air buoyancy, convection effects within the furnace, crucible geometry, radiation effects, the atmosphere in the furnace and the fact that the crucible support is subject to a temperature gradient within the furnace. It is necessary to use the apparent weight change of the empty crucible as a correction curve to arrive at the actual weight change occurring in a sample.   This is considered to be more satisfactory than the use of a tare crucible, as has been proposed,[31] in a separate furnace, in view of the possible non-uniformity of the hot zones in the two furnaces.

Since several factors contribute to this correction curve it is found that the corrections to be applied differ with different rates of heating.   Various workers[12,32,33] have discussed the factors affecting the correction curves, and Duval[34] and Newkirk[12] have suggested the use of vents at the top of the furnace to reduce the size of the correction.   This has been criticised[32] as amounting to critical damping of the hot-zone volume.   Empirical equations have been derived[35,36,37] for the correction curves, but because of the complexity of factors involved it seems simpler to use a correction curve determined practically under conditions identical to those of the actual experiment.

FACTORS AFFECTING THE RESULTS OBTAINED—

There are several factors that may, to a greater or less extent, influence the shape of a corrected thermogravimetric curve for a particular compound.

Heating rate—For a single-stage endothermic reaction, where T_1 is the procedural decomposition temperature and T_f is the temperature at which the reaction is completed, it has been shown[5,38,39,40] that—

(i) $(T_f)_f > (T_f)_s$,

where the subscripts f and s refer to a fast and slow rate of heating, respectively,

(ii) $(T_1)_f > (T_1)_s$ and

(iii) $(T_f - T_1)_f > (T_f - T_1)_s$.

Newkirk[12] has shown that, at any given temperature, the extent of decomposition is greater at a slow rate of heating than for a similar sample heated at a faster rate.   If the reaction involved is exothermic, the sample temperature will rise above the furnace temperature; it has been shown (in unpublished work by us) that the difference between the furnace temperature and the sample temperature is greatest for the faster rate of heating when a reaction is occurring.   When successive reactions are involved, the rate of heating may well determine whether or not these reactions will be separated.   The appearance of a point of inflection in the thermogravimetric curve at a fast heating rate may resolve into a plateau at a slower heating rate.[23]   The importance of heating rates was stressed by early workers[41,42] and has been much studied.[43 to 47]

Sample—The sample weight can affect the thermogravimetric curve in three ways—

(i) The extent to which endo- or exothermic reactions of the sample will cause the sample temperature to deviate from a linear rise; in general, all other factors being equal, we have found that the greater the weight of sample, the greater will be the deviation.

(ii) The degree of diffusion of the product gas through the void space around the solid particles; under static conditions, the environmental atmosphere (*i.e.*, the atmosphere immediately surrounding the reacting particles) will be somewhat governed by the bulk of the material in the crucible.

(iii) The possible unevenness of the temperature throughout the sample, particularly if it has a low thermal conductivity.

Thus the use of as small a weight of sample as possible, within the limits of the sensitivity of the balance, is to be preferred.

The state of sub-division of the sample is important.   The use of large crystals may result in spitting, as described by C. J. Keattch in a private communication.   The sample may foam and bubble.[48]   Most thermogravimetric studies have been carried out on powders, and the effect of particle size or surface area has been widely studied.[41 to 52]   The smaller the

particle size the greater the extent to which equilibrium is reached, and at any given temperature the extent of decomposition is greater.

The pre-history of the sample is also important. Wendlandt[53] has discussed the effect of precipitation technique on the thermogravimetric curve of ammonium molybdophosphate. Recent work on magnesium hydroxide from different sources provides a good illustration of this factor.[54]

Crucible—The geometry of the crucible used will profoundly affect the shape of the thermogravimetric curve. Crucible design has been studied,[55,56] and the use of a crucible fitted with a piston (where reactions take place under a pressure of 1 atmosphere of the liberated gas) or an on open tray (at the partial pressure of the gas in the atmosphere) have been compared. This latter arrangement has been used by other workers.[57,58] The design of a crucible to overcome possible condensation on the support rod or decrepitation before decomposition has also received attention.[59,60] In certain instances the material of which the crucible is constructed affects the decomposition pattern.[61]
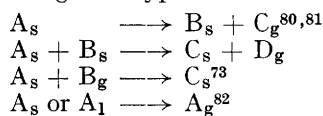
Atmosphere—

(*i*) *When the atmosphere does not take part in the reaction*—The use of an inert atmosphere in thermogravimetric analysis has been discussed.[59] The rôle of the gas is to remove gaseous products from the vicinity of the sample, to ensure that the environmental atmosphere is kept as constant as possible throughout the experiment and to prevent reaction occurring between the sample and air as normally employed,[62,63] or between the volatile components and the atmosphere.[5,59] Other workers[64 to 68] have used vacuum conditions to achieve the same results. The dependence of the shape of thermogravimetric curves on the pressure of the gas in the reaction chamber has been studied.[69]

(*ii*) *When the atmosphere is involved in the reaction*—Some work has been carried out with atmospheres either of humidified air or high pressure steam[12,70,71]; a dynamic air atmosphere has been used to study the roasting of copper sulphide[43] and the oxidation of reduced iron catalyst.[72] A comparison of some six atmospheres in metal-gas reactions has been made by Markowitz and Boryta.[73,74] Reducing atmospheres, *e.g.*, hydrogen, have been used.[75,76,77] Other atmospheres, in which reactions occur between the gas and the sample, that have been studied include hydrogen sulphide[78] and carbon dioxide.[79]

KINETIC STUDIES

Thermogravimetric data can be used to evaluate kinetic parameters of reactions involving weight loss (or gain) of the following four types—

$$A_s \longrightarrow B_s + C_g^{80,81}$$
$$A_s + B_s \longrightarrow C_s + D_g$$
$$A_s + B_g \longrightarrow C_s^{73}$$
$$A_s \text{ or } A_l \longrightarrow A_g^{82}$$

The advantages of determining kinetic parameters by thermogravimetric methods rather than by conventional isothermal studies are (*i*) considerably less data are required than in the isothermal method, (*ii*) the kinetics can be probed over an entire temperature range in a continuous manner and (*iii*) when a sample undergoes considerable reaction in being raised to the required temperature, the results obtained by an isothermal method are often questionable. To these reasons may be added the advantage of using one single sample in the study.

It is important to know the temperature accurately and to ensure that endo- or exothermic effects do not cause the rate of heating to depart from its constant value.[73] The use of small samples, within the limits of sensitivity of the balance, is therefore necessary. It should be remembered that kinetic parameters derived from thermogravimetric experiments are dependent on the procedural details, *e.g.*, crucible shape and material, particle size, pre-history of sample and heating rate.[47,54]

The earliest attempt to use thermogravimetric curves for kinetic data appears to have been made by Van Krevelen, Van Heerden and Huntjens.[83] They derived an approximate equation, from which it was possible by graphical methods to determine the order of reaction (they differentiated between orders of 0, 1 and 2). They studied the pyrolysis of coal and showed that the primary decomposition was first order. On this assumption they developed graphical methods for determining the activation energy and frequency factor, knowing the rate of heating, temperature of maximum rate of decomposition and the half-value width of the differential thermogravimetric curve.

Kaesche-Krischer and Heinrich[47] used a similar approach in their study of the pyrolysis of poly(vinyl alcohol) in a vacuum, and Schnitzer, Turner and co-workers[84,85] studied the organic matter of Podzol soils. Turner, Hoffman and Chen[54] modified Van Krevelen's approach to accommodate a two-thirds order in their work on the thermal decomposition of magnesium hydroxide.

Freeman and Carroll[80] derived the equation—

$$-\frac{E/2\cdot 3R\Delta T^{-1}}{\Delta\log W_r} = -x + \frac{\Delta\log(dw/dt)}{\Delta\log W_r} \qquad .. \qquad .. \qquad .. \qquad (1)$$

where E = activation energy, R = general gas constant, T = absolute temperature, x = order of reaction and $W_r = (W_c - W)$, where W = weight loss at time t, and W_c = weight loss at completion of the reaction. This equation was derived by assuming a rate expression—

$$-\frac{dX}{dt} = kX^x \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

where X = amount of A at time t and the rate constant, k, is given by the simple Arrhenius expression—

$$k = Ze^{-E/RT} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

where Z = frequency factor. Either by plotting a graph of $\dfrac{\Delta\log(dw/dt)}{\Delta\log W_r}$ *versus* $\dfrac{\Delta T^{-1}}{\Delta\log W_r}$ or by other suitable rearrangement of equation (1)[64,81,86] it is possible to derive values for both E and x.

This derivation has been used to study several dehydration reactions.[7,58,80,81,87 to 91] Barrer and Bratt[92] have used an adaptation of equation (1) in their study of non-stoicheiometric hydrates. The decomposition reactions of calcium oxalate,[80,81] thorium, lanthanum and uranium oxalates,[93] calcium carbonate,[80,81] chromium arsenate[58] and 12-tungstomanganic acid[94] have all been studied. Bear and Wendlandt[95] have studied the effect of added salts on the decomposition of trisethylenediamine and trispropylenediamine chromium[III] chlorides and thiocyanates. Similarly, the pyrolysis of several polymers has been studied[64,86,96,97] However, several disadvantages appear to exist in the use of this derivation—

(*i*) in most practical instances the derivation seems to apply to an extremely limited portion of the decomposition curve;

(*ii*) there is considerable difficulty in obtaining a reliable value for the order of reaction;

(*iii*) none of the other methods of applying the derivation seems to overcome the difficulties; and

(*iv*) in certain reactions the method does not seem to yield an answer at all[87]—this may be due to the reaction itself and not inherent in the derivation.

In his method,[12] Newkirk assumes that all pyrolytic decompositions are first order, and his method involves calculating the first-order rate constants for a large number of temperatures, and then constructing the Arrhenius graph. In his study of Mylar (a plastic marketed by Du Pont Company Ltd.) he showed that the slope of the graph was independent of heating rate, but, as the rate of heating was increased, the graphs were displaced towards lower values of $1/T$, compared with the results obtained from isothermal studies. Smith[98] has used a similar approach to derive E_p (E_p denotes that E, the activation energy, may be somewhat dependent on the experimental procedure) for various polymers.

Other workers[44] have determined apparent activation energies by plotting the reciprocal of the final decomposition temperature against the logarithm of the heating rate.

Doyle[82] integrated a combination of expressions equivalent to equations (2) and (3), using an approximation. His technique is essentially one of curve fitting. He studied the zero-order volatilisation of liquid octamethylcyclotetrasiloxane and the first-order pyrolytic volatilisation of polytetrafluoroethylene. He confines himself to zero- or first-order reactions, but his approach cannot be used when the order is unknown.

Horowitz and Metzger[99] have recently developed another approach based on integration of a combination of expressions equivalent to equations (2) and (3) by an exact integral, using the substitution $(T - T_s) = \theta$ where T_s is the temperature at which $\dfrac{W}{W_0} = \dfrac{1}{e}$, ($W$ = weight of sample at time t, and W_0 is the initial weight of the sample). The theory

shows that a plot of $\ln$ ($\ln \dfrac{W_o}{W}$) *versus* θ should be a straight line of slope $\dfrac{E}{RT_s{}^2}$. These workers have studied four polymers and the dehydration of calcium oxalate monohydrate. In each reaction they assume a particular order of reaction. For an unknown order they suggest the use of the position of maximum rate since this is governed by the order. It is, however, not always easy to determine the position of maximum rate with accuracy.

Coats and Redfern[100] used a different approximation for integrating a combination of equations (2) and (3). The graph of

$$\log \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} \ versus \ \frac{1}{T}$$

is a straight line of slope $- E/2 \cdot 3R$ for the correct value of n ($\alpha = $ fraction decomposed and $n = $ order of reaction).

The activation energy can have a real meaning in solid-state kinetics, corresponding to the rate-determining step or steps, which might be the diffusion of the gaseous product out of the solid, or the transport of a particular ion, or the breakage of bonds. The order of reaction cannot presumably have the meaning attributed to it, as in a gas reaction, and may best be considered as a mathematical factor in the derived equations. However, geometric models of solid systems that lead to orders of reaction of $\frac{1}{2}$ and $\frac{2}{3}$ can be set up[101]; orders of 0 and 1 can also be justified.

Two points remain. The first is a plea for the use of standard symbols in the description of kinetic processes (see, for example, Garner[102]). The second is that it seems unlikely that the simple rate expression $\dfrac{d\alpha}{dt} = k(1 - \alpha)^n$, from which all the derivations quoted are ultimately derived, will be applicable to all solid-state decomposition reactions.

The use of computational methods for analysing thermogravimetric data is probably in wider use than the number of papers on this subject would suggest.[100,103] The advantages that these methods possess in assisting in the evaluation of kinetic parameters are obvious; their more widespread introduction will undoubtedly lead to a better coverage of some of the necessary studies on the effect of the variables, listed under "Techniques," on kinetic parameters.

APPARATUS

The comprehensive review of Gordon and Campbell[19] covered the whole field of automatic and recording balances up to 1959. Many of these are directly applicable or readily adaptable for use in thermogravimetry. Lewin[20] discusses six makes of commercial thermobalances on the market in 1962 and lists another four firms manufacturing thermobalances. Duval[18] puts the number of thermobalance models on the market at fifty-two. Other firms[104,105,106] known to us are manufacturing thermobalances.

The essential components of a modern thermobalance are: (*i*) balance, (*ii*) furnace, and (*iii*) recorder. It is desirable to have a reaction chamber to permit work to be carried out under a wide variety of conditions, *e.g.*, inert, oxidising or reducing atmospheres or under vacuum, and to permit gas analysis to be carried out. The balances used can be grouped into two types. They are the null-point and the deflection types of instruments. The former incorporates a suitable sensing element that detects any deviation of the balance beam and the application of a restoring force, proportional to the change in weight, to return the beam to its original null-point. This restoring force is then recorded either directly or through a transducer. These null-point type instruments are often readily adaptable to working under vacuum conditions. Deflection instruments, *e.g.*, based on a conventional analytical balance, a helical spring, a cantilever beam, a strain gauge or a torsion balance, involve the conversion of deviations into a record of the weight change. The principles used in detecting and restoring deviations (in null-point balances), and in recording the changes in weight have been fully discussed.[19]

Furnace design and control is of great importance; it must be designed to provide a suitable smooth input so that it can maintain a linear heating programme or a fixed temperature, independent of any changes in external conditions. The comments on temperature control in differential thermal analysis[3] apply equally to thermogravimetric analysis. Control is generally achieved via a thermocouple situated as close to the furnace winding as possible.

The appearance of thermal pulsing effects owing to the periodic application of relatively large power increments leads to a ragged weight record,[32] and the use of some form of stepless control of power supply to the furnace through a saturable reactor is to be preferred.[107] Nichrome winding permits a maximum temperature of around 1100° C; platinum - rhodium winding permits a maximum of around 1450° C. Higher temperatures can be achieved by using a graphite tube furnace, but the associated control and measurement of temperatures raise considerable problems.

The recording system should be able to record both temperature and weight continuously and to make a periodic record of the time. The use of "$X_1 - X_2$"[105] or side-by-side[108] recording is to be preferred to the use of "X — Y" recording,[5] since these methods provide an independent record of both temperature and weight.

The prospective user has a variety of instruments available over a wide cost range. His choice should reflect the requirements of his particular field of study and the desiderata for good thermobalance design (see, for example, Lukaszewski and Redfern[23]), namely that—

(*i*) The thermobalance should be capable of continuously registering the weight change of the sample studied as a function of temperature (and time).

(*ii*) The furnace should be capable of reaching the maximum temperature desired. Most commercial instruments are marketed with a maximum of around either 1100° or 1500° C (some thermobalances are available and have been designed to work up to 2200°[105] or 2700° C[109]).

(*iii*) The rate of heating is truly linear and is reproducible.

(*iv*) The hot zone of the furnace is as near uniform as possible, and that the crucible is always located within this hot zone. This is particularly important in deflection instruments, since the crucible will move in relation to its initial position in the hot zone during the course of the run.

(*v*) The instrument is as versatile as possible, providing for—

    (*a*) variation in heating rate,

    (*b*) heating in a dynamic flow of a controlled atmosphere, inert, oxidising or reducing,

    (*c*) heating *in vacuo*,

    (*d*) variation in chart speed to aid interpretation and

    (*e*) the possibility of carrying out accurate isothermal studies.

(*vi*) Physical effects (*e.g.*, radiation and convection currents, and magnetic effects caused by the winding of the furnace) due to the functioning of the apparatus do not upset the balance mechanism. No interaction should occur between conducting or magnetic samples being studied and the furnace winding. Possible chemical attack, from the gases used or the gases evolved, can be eliminated either by the design of the reaction chamber or by the materials used. The balance mechanism is sufficiently protected from the furnace, so that its sensitivity remains constant throughout the whole of the experimental run.

(*vii*) The temperature of the sample is measured as accurately as possible.

(*viii*) The sensitivity of the balance mechanism allows the study of small samples.

Several workers have described the construction of relatively simple inexpensive instruments, *e.g.*, those suitable for teaching the principles of the subject or for preliminary studies.[22,110,111,112] Micro-recording,[113,114] vacuum or controlled-atmosphere[112,114,115,116] thermobalances have been described in detail. Recent papers, in which automatic thermobalances[117 to 121] are described, include details of models capable of operating up to 40[117] and 60[118] atmospheres. In view of the trends in current instrument design reviewed by Eastwood,[122] the development of an automatic digital-recording thermobalance is of great interest.[123] There is considerable activity in the development of instruments capable of performing both thermogravimetric and differential thermal analysis either on the same sample or under similar conditions.[46,107,124,125,126] However, it should be borne in mind that the conditions for producing meaningful results are not necessarily the same for both techniques, although comparison is often valuable and, in some instances, essential.

Several workers have described modifications to existing commercial recording balances or thermobalances. Thus the Ainsworth recording balance has been incorporated in a thermobalance design[31]; the Stanton thermobalance has been adapted for work in atmospheres of hydrogen[127] and for producing the differential thermogravimetric curve.[10]

It is possible to measure the sample temperature directly without affecting the performance of a conventional balance by means of extremely fine connecting wires (of about 0·001-inch diameter) between the balance arm and a suitably located terminal block. The thermocouple wires then run up the support rod the crucible, and the bead may be located in or close to the sample, depending on the design of the crucibles used.[46,108]

APPLICATIONS

ANALYTICAL CHEMISTRY—

The widest application of thermogravimetric analysis to date has been in the investigation of analytical procedures: (*i*) in investigating suitable weighing forms for many elements; (*ii*) in testing materials that are actual or potential analytical standards; and (*iii*) in the direct application of the technique to analytical determinations.

Kobayashi[128] has reviewed the work of the Japanese School from 1925 to 1940 in the field of gravimetric analysis; from some twenty-seven references he listed about 300 precipitates and gave the recommended drying temperatures. In the first edition of his book,[129] Duval reported his studies on over 1000 gravimetric precipitates for nearly 70 elements. He concluded that only about 200 of these are suitable weighing forms for the elements. Erdey's book[130] on gravimetric analysis includes thermogravimetric, differential thermogravimetric and differential thermal analysis curves obtained on the Derivatograph[9] for each weighing form discussed. Two reviews have been published.[131,132]

There has been criticism of some of Duval's work on a number of grounds. Differences between other published work and that of Duval and his co-workers has been ascribed to different precipitating techniques,[53] to different washing techniques,[133] and to the use of high rates of heating.[134] Duval's criterion for rejecting a particular gravimetric precipitate as not being a suitable weighing form was that it did not give a plateau when heated at one particular rate of heating. Newkirk[12] refers to the investigation of zinc monosalicylaldoxime in which de Clercq and Duval,[135] using the method of Flagg and Furman[136] to prepare the precipitate, found no plateau on the thermogravimetric curve corresponding to the anhydrous compound. Detailed work by Rynasiewicz and Flagg[137] showed that the anhydrous form was stable from ambient temperature up to 285° C; further, that the plateau depended on the initial water content. Newkirk continues: "In as much as Duval has used a higher heating rate (ca. 380° C per hour), it is perhaps not surprising that he failed to find a plateau. The rejection of this precipitate as an analytical method for the determination of zinc on the grounds that it does not give a stable horizontal in the thermobalance at one particular rate of heating is clearly unwarranted. . . . The results suggest that when the thermobalance is used to study the drying of bulky precipitates that contain considerable water, it would be well to use very slow rates of heating."

The use of thermogravimetric data to interpret the best drying temperature (a constant temperature) must be made with a clear understanding of the dynamic nature of the technique. Regard must also be paid to all the factors mentioned in the section on "Techniques." It is clear that failure to do this may lead to considerable difficulty and controversy. To summarise—

    (*i*) The lack of the appearance of a plateau, at one particular heating rate, is insufficient evidence on which to judge the suitability or otherwise of a particular weighing form.

   (*ii*) The appearance of a plateau is not conclusive evidence that the weighing form is isothermally stable at all or any of the temperatures that lie on the plateau.[5]

  (*iii*) It is evident that the most reliable information will be gained by using several different heating rates or, at least, a slow rate of heating, possibly with preliminary air drying.

However, there is much to be gained from a thermogravimetric investigation of a weighing form since the recommended temperatures for some procedures have been arrived at arbitrarily, and have frequently been quoted in the literature without any critical evaluation of the conditions required. Beamish and McBryde[138] have shown that certain instructions given

for the heating or ignition of materials in some gravimetric determinations were quite inadequate.

Recent investigations include the study of: ammonium molybdophosphate[53] and quinolinium molybdophosphate[139] as suitable weighing forms for phosphorus; several sulphides[140] and selenides[141] to confirm methods of drying and weighing; lanthanum carbonate[142] and lanthanum oxalate[143] to find suitable weighing forms for lanthanum; the use of m-nitrobenzoic acid as a precipitant for cerium^{IV} [144]; and various compounds of plutonium to find suitable weighing forms for it.[145,146] Picrates and styphnates of some organic bases, such as guanidine and related compounds, have been examined since these derivatives are constantly used in characterisation and analysis.[147]

Thermogravimetric studies have been made of many substances of use or of potential use as standards in analysis. Thus a series of papers by Duval has appeared on the use of this technique in conjunction with infrared spectra.[148,149] Investigations of potassium hydrogen phthalate,[150] ethylenediaminetetra-acetic acid (EDTA) and its derivatives,[151] some tetraphenylboron salts of oximes[152] and 5-substituted barbituric acids[153] have been carried out.

It has been shown that soils can be analysed thermogravimetrically for determining hygroscopic moisture, organic matter, and inorganic carbonates.[154,155,156] Dupuis and Dupuis[157] have used thermogravimetry for determining calcium and magnesium in dolomite rock. The use of thermogravimetry in the study of the composition of non-interacting binary mixtures has been outlined.[23] Erdey and co-workers,[158,159] using the Derivatograph, have determined calcium, strontium and barium in a single sample by their precipitation as the mixed hydrated oxalate, using the losses of weight of extraneous water and water of crystallisation, and loss of carbon monoxide and dioxide. Berlin and Robinson have used thermogravimetry in their determination of magnesium, potassium and lead with dilituric acid[160] and for determining ethylenediamine and quinine,[161] with the same precipitant. Fluorine has also been determined thermogravimetrically.[162]

INORGANIC CHEMISTRY—

In recent years the greatest number of papers on thermogravimetric analysis has appeared within the field of inorganic chemistry. In a review of this nature it is not possible to discuss the work in detail; however, an attempt has been made to collate recent work on the basis of the anion of the compound studied. Studies of inorganic compounds are concerned with their stability, decomposition and structure. The types of reaction that have been observed are—

(i) Loss of constituent water molecules; such dehydrations may be either single or multi-stage, and may involve the loss of the elements of water, e.g., from hydroxyl groupings.

(ii) Decomposition reactions, which may be either of a disproportionation or of a degradation type. Brill,[163] in what was probably the first publication in the field of thermogravimetry, presented data of this degradation type. He studied the decomposition of magnesium; calcium and barium carbonates—

$$M^{II}CO_3 \longrightarrow M^{II}O + CO_2.$$
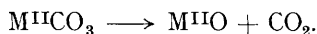
(iii) Degradation reactions specifically involving the atmosphere, for example, oxidative degradation. An example is provided by the oxidation in air of trispropylenediamine chromium^{III} chloride—

$$2[Cr(pn)_3]Cl_3 \xrightarrow{\text{air}} Cr_2O_3 + \text{volatiles.[164]}$$
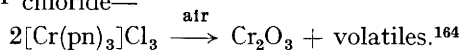
(iv) Loss of constituent volatile ligands from inorganic complexes. An example is provided by the loss of ethylenediamine from trisethylenediamine chromium^{III} chloride—

$$[Cr(en)_3]Cl_3 \longrightarrow [Cr(en)_2Cl_2]Cl + en.[95]$$
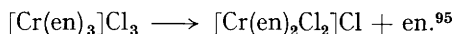
Though it has been clearly demonstrated that the thermal decomposition of inorganic compounds is dependent on the nature of both anion and cation, there has been little attempt to relate thermal decomposition data to modern theories in inorganic chemistry. Wendlandt[165] found a linear relationship between the ionic radii of the alkali metal ions and the temperature at which their tetraphenylboron salts began to decompose. Others have proposed reaction schemes to account for the pattern of thermal decomposition.[58,95,166,167]

Anions derived from elements of Group III—Some borates of lithium and sodium have been studied.[168] The decomposition of some calcium aluminate hydrates[169] and calcium carbo-aluminate[170] has been investigated, that of the former under constant water vapour pressure.

Anions derived from elements of Group IV—

(*i*) *Carbonates*—Freeman[81] has studied the kinetics of the decomposition of calcium carbonate, comparing results obtained with results from isothermal studies. Lanthanum carbonate has been investigated as a suitable weighing form for lanthanum[142]; other lanthanon carbonates have been studied.[171,172] The effect of crucible design on the decomposition characteristics of lead carbonate has been studied.[173] Other recent studies on carbonates include ammonium scandium carbonate[174] and certain cobalt[II] complex carbonates.[175] Thermogravimetric studies of solid-state reactions between cerium oxide, neodymium oxide or samarium oxide with either sodium carbonate or sodium sulphate,[176] and of the strontium carbonate - zirconium oxide and barium carbonate - zirconium oxide systems have been made.[177] Wilburn and co-workers[8,178] have studied the systems sodium carbonate - silica and calcium carbonate - silica, by both thermogravimetric and differential thermal analysis and discussed their behaviour in relation to glass manufacture.

(*ii*) *Formates, acetates, oxalates and other oxycarbon anions*—Copper[II] formate[179] and aluminium acetate[180] have recently been investigated. However, oxalates have received a great deal of attention, *viz.*—those of copper,[67] beryllium,[181] magnesium,[182] calcium,[5,80,81] zinc,[67] cadmium,[67] lead,[67] manganese[II],[67] cobalt,[173] nickel,[67,182] scandium,[183] yttrium,[183] lanthanum,[68,93,143,183] other lanthanons,[68,172,184,185] thorium[93] and uranium,[93,186] complex cobalt oxalates,[175] oxalato-niobates[187] and other complex oxalates.[188] The additivity of the decomposition curves of a mixture of oxalates has been demonstrated,[182] and the thermal decomposition pattern of oxalates in different atmospheres has received attention.[5,189] Other compounds of oxycarbon anions that have been studied include potassium hydrogen phthalate,[190] caesium propionate, butyrate, and isovalerate[191] and lanthanum and cerium[III] palmitate, laurate and stearate.[192]

(*iii*) *Silicates*—The dehydration behaviour of several silicates and silicate minerals has been investigated.[193 to 198] The use of thermogravimetry combined with infrared studies has been suggested to permit a distinction to be made between constitutional and adsorbed water.[199] The effect of alkaline-earth chlorides on the dehydration of silica Xerogel has been studied.[200]

(*iv*) *Others*—Thermogravimetry has been used to determine the conditions under which calcium orthoplumbate[IV] is formed.[201]

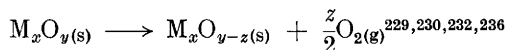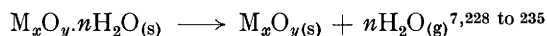## Anions derived from elements of Group V—

(*i*) *Nitrogen*—The reaction between boron oxide and sodamide to yield boron nitride[202] and the oxidation of aluminium nitride[203] have been studied thermogravimetrically. The thermogravimetric behaviour of cerium[III,204] praseodymium, neodymium, samarium,[172] thorium,[205,206] plutonium[146] and nickel[207] nitrates has been investigated. Lead azide has been studied.[208]

(*ii*) *Phosphorus*—The resistance to oxidation of some transition metal phosphides[209] has been described. Phosphates of ammonium,[210] sodium,[211] beryllium,[212] calcium,[213,214] strontium,[214] cadmium,[214] aluminium,[215,216] antimony,[217] chromium[166] and iron,[215,216] and some halophosphates have been studied.[218,219,220] The decomposition of disodium dihydrogen pyrophosphate[221] and the reactions between magnesium pyrophosphate and strontium oxide or magnesium hydroxide[222] have been reported. Gerrard, Mooney and Rothenbury have used thermogravimetry in their investigation of polymers formed from chloroborazoles and phosphorus esters.[223]

(*iii*) *Other anions*—Arsenic acid[224] and arsenates of chromium,[58] cobalt[225] and nickel[225] have been investigated thermogravimetrically. Ammonium metavanadate,[226] some niobates and tantalates[227] and some oxalato-niobates[187] have also been studied.

Anions derived from elements of Group VI—

(*i*) *Oxides, peroxides and related compounds*—Thermogravimetric studies of oxides may be sub-divided into two main sections: (*a*) Dehydration reactions of hydrated oxides and subsequent disproportionation reactions—

$$M_xO_y.nH_2O_{(s)} \longrightarrow M_xO_{y(s)} + nH_2O_{(g)}^{[7,228 \text{ to } 235]}$$

$$M_xO_{y(s)} \longrightarrow M_xO_{y-z(s)} + \frac{z}{2}O_{2(g)}^{[229,230,232,236]}$$

(*b*) Solid-state reactions, which may be either solid - solid reactions involving loss of volatiles,[8,176,177,178,202,222,237,238,239] or solid - gas reactions involving loss or gain in weight,[76,240,241] have also been reported. The thermal dehydration of copper,[242] beryllium,[181] magnesium,[54] iron[III 243] and nickel[193] hydroxides has been investigated thermogravimetrically. On the basis of thermogravimetric and infrared methods several metal oxyhydrates have been classified into four groups.[244]

(*ii*) *Sulphides, sulphates and other anions of sulphur*—The oxidation and thermal decomposition of copper,[43,245] zinc,[245] cadmium,[245] mercury,[245] germanium,[246] tin,[245] lead,[245] and various nickel sulphides[247,248,249] has been described, and there have been two studies on pyrites.[50,250] Sulphates of the metals listed below have been studied: copper,[245,251] beryllium,[181] magnesium,[252] calcium,[253] zinc,[245] cadmium,[245,254] mercury,[245] indium,[255] tin,[245] lead,[245] nickel,[256] uranium,[257] lanthanum,[258,259] and other lanthanons,[172,259] as well as several double and complex sulphates.[252,260 to 263] Solid - solid[264] and solid - gas[265] reactions involving sulphates have also been reported. Rocchiccioli[266] has studied the decomposition of sulphamic acid and some metal sulphamates.

(*iii*) *Anions derived from the other elements of Group VI*—The selenides of arsenic, rhenium and mercury have been shown to sublime at definite temperatures.[141] The decomposition of magnesium selenates has been compared to the corresponding sulphates.[252] The thermal decomposition of neodymium and basic yttrium chromate has been studied,[267] as well as some isopolychromates of potassium.[268] Tungstic acid,[269] ammonium paratungstate,[269] several 12-heteropoly tungstates,[89,90,94] ammonium[53] and quinolinium molybdophosphate[139] have been investigated thermogravimetrically.

Anions derived from elements of Group VII—Thermogravimetric studies of mono-amine dichloro zinc[270] and basic aluminium chlorides[271] have been made. A study of the application of high temperature thermogravimetry of chlorides and sulphates to soil analysis has been reported.[272] $CdI_2.xNH_3$[273] and some tetra-iodomercurates[274] have been investigated. The thermal decomposition of the following compounds involving oxyanions has been reported: sodium chlorite,[275] barium bromate[276] and chlorate[276] and copper[II] iodate,[276] together with the perchlorates of potassium,[48] magnesium,[277] calcium[277] and barium.[276,277] Binary systems of potassium perchlorate with either alkaline or alkaline-earth metal nitrates,[278] and the course of the reaction between potassium chlorate and manganese dioxide[279] have been followed by using thermogravimetric techniques.

Barium permanganate[280] and ammonium perrhenate[281] and the compounds $AgMn_2O_4$ and Ag_2MnO_2[282] have been studied by using a thermobalance.

Anions derived from elements of Group VIII—Alkali metal,[283] copper,[284] magnesium[285] and alkaline-earth[285] ferrocyanides have been examined by Seifer. Work on ammonium chloroplatinate[286] and bromoplatinic acid[287] has also been reported.

Complex inorganic compounds—Complex compounds of cobalt, chromium, nickel and platinum in which the ligand groups are wholly or partly either ammonia, ethylenediamine, propylenediamine or pyridine have been widely studied by Wendlandt and his school[95,175,288 to 292] and also by others.[167,293,294] The 8-hydroxyquinolines of many bivalent metals,[295,296] uranium[297] and plutonium[145] have been studied. Bivalent metal anthranilates,[298] substituted anthranilates of lanthanum and lead,[299] and other related chelate complexes[88,300,301] have all been studied thermogravimetrically. Other work on complexes has been carried out by Wendlandt and co-workers,[302,303,304] Charles[305] and Dhar and Basolo.[306] Clathrates of the type $Ni(CN)_2.NH_3 X$, where X = benzene, thiophen, pyrrole, furan or phenol,[307] have been examined by using a quartz-spring thermobalance.

ORGANIC CHEMISTRY—

The application of thermogravimetric analysis to organic compounds is best discussed under two headings.

Synthetic organic polymers—These have been much studied in recent years, particularly with the advent of apparatus in which the sample can be heated in an inert atmosphere or under vacuum.   Since the breakdown of polymers into the volatile monomer units is nearly always a simple single-stage process, these reactions have been used as standards in non-isothermal kinetics (see "Kinetic Studies").[64,82,96,97,99] H. C. Anderson has compared differential thermogravimetry with differential thermometry as a method for studying the pyrolysis of polymers.[308]   Recently Doyle[309] has derived equations from which it is possible to determine the isothermal life of polymers from thermogravimetric data.   Table I lists some polymers that have been studied by a thermogravimetric technique.

TABLE I

SYNTHETIC POLYMERS STUDIED BY THERMOGRAVIMETRY

Polymer	References—	
	Kinetics studied	Kinetics not studied
Epoxide polymers	97	65, 310
Polyamides	311	—
Polyethylene	64, 99	312
Polymers based on methyl methacrylate	99	52
Polypyromellitimides	—	63
Polystyrene	64	—
Poly(t-butyl acrylate)	313	—
Polytetrafluoroethylene	82, 96	310, 314
Poly(vinyl alcohol), PVA	47, 315	—
Poly(vinyl chloride), PVC	316	62, 310
Other vinyl polymers	—	317
Phenolic polymers	—	318 to 320
Silicones	—	310
Urea - formaldehyde resins	—	321

Other organic compounds—Few simple organic compounds have been studied.   Duval[322] has investigated the thermal stability of some organic compounds used as analytical standards. Other compounds studied include EDTA,[151] barbituric acid and related compounds.[153] Some organo-tin compounds have been investigated by thermogravimetry.[323]   The pyrolysis behaviour of several coals, peats and bitumens has been studied[324 to 327]; their kinetics of decomposition has also received attention.[83,328]   The mechanism of thermal decomposition of some organo-montmorillonites has been investigated.[329]   Thermogravimetric and differential thermal analytical studies have been made of the pyrolysis of wood and of wood treated with inorganic salts.   Some conclusions regarding the action of salts that are flame retardant are discussed.[330,331]   There have been two studies on inclusion or clathrate compounds. McAdie[332] has studied the urea - n-paraffin inclusion compounds, and Gilford and Gordon[67] have examined the behaviour of some quinol clathrates under ambient and reduced pressures.

COMPLEMENTARY PROCEDURES

We have reviewed the various applications of thermogravimetric analysis, but there has been little stress on the fact that, in many of the papers referred to, other techniques have been used to complement the information gained from thermogravimetry.   In certain investigations, it is essential to use a complementary technique if the interpretation of the course of a thermal decomposition is not to be pure guess-work; at least, chemical analysis of the solid removed from the thermobalance at an appropriate point on the thermo-gravimetric curve[58] or, alternatively of the evolved gas[316] should be carried out.   Information gained from thermogravimetry becomes more meaningful or can readily be extended by the use of techniques that are applicable to solid-state chemistry.[25]   It is not the object of this review, however, to discuss these procedures in detail but to offer a few pertinent comments.

DIFFERENTIAL THERMAL ANALYSIS—

This method is taken first, owing to its close affinity to thermogravimetry (see Introduction, p. 906).   Both are dynamic methods, and both are very much dependent on procedural details.[3]   It is not true that what is good technique for thermogravimetric analysis

is necessarily so for differential thermal analysis. There is no doubt that much useful and meaningful information can be obtained with equipment designed to carry out both thermo-gravimetry and differential thermal analysis at one and the same time on the same sample—the success of the Derivatograph[9,50,158,159,210,243] is proof of this. Nevertheless, there are limitations. For example, in differential thermal analysis the sample is generally packed down in the crucible[3] so that the energy changes occurring in the course of the reaction produce a "good" peak; hence, again, the use of higher rates of heating in differential thermal analysis. For quantitative thermogravimetry, however (particularly if evaluation of kinetic parameters of the reaction is to be attempted), both of these operations would not be considered good practice. Garn[173] has discussed various aspects of this problem. An apparatus, such as that described by Hodgson,[107] offers a compromise, in that both procedures are available to the operator but as completely independent operations. The use of the two procedures permits information to be obtained on all phenomena listed on p. 906. Examination of a material by both procedures permits crystalline transitions, second-order transitions and solid - solid reactions occurring without weight change to be distinguished from a typical decomposition reaction, or indeed any of the phenomena listed on p. 906 that give rise to a weight change.

OTHER PROCEDURES—

In many of the studies discussed, one of the main uses of thermogravimetry has been the investigation of the thermal stability of the material,[13,149,322] or to find a suitable drying temperature for the investigation of a weighing form of an element.[143 to 146] However by using thermogravimetry together with infrared studies, X-ray diffraction[21] or electron-diffraction studies, or magnetic measurements—say, by heating up to a suitable point on the thermo-gravimetric curve (up to a point where a reaction has occurred) and removing the sample for examination by one or more of these methods—information can be gained on what structural changes have occurred during the course of the reaction. Thus a combination of infrared studies and magnetic measurements with a detailed thermogravimetric examina-tion of the dehydration of hexa-aquochromium[III] phosphate and arsenate enabled Lukaszewski and Redfern[58,166] to propose a reaction scheme for the dehydration reactions. A thermogravimetric study, coupled with X-ray diffraction studies and a study of catalytic activity,[7] of a hydrated ruthenium dioxide provided preliminary information on some structural changes occurring on heating.

CONCLUSION

It is evident from the volume of literature now appearing[1] that both thermogravimetric and differential thermal analysis have found many varied applications both in analytical chemistry and in other fields. It is likely that the introduction of more sophisticated instru-mentation (with facilities for operating in inert, oxidising or otherwise controlled atmospheres) will lead to further developments, particularly in the fields of organic and inorganic materials and to the use of thermogravimetry directly as an analytical method. It is to be hoped that prospective workers in the field will realise the dynamic nature of the method and of its dependence on the factors outlined in the section on "Techniques."

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