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THE ANALYSIS OF THERMAL DATA*

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ABSTRACT

The thermal analysis of simple endothermic solid state decomposition reactions at either fixed or programmed furnace temperatures can yield precisely analyzable data. Rigid experimental controls are dictated by mathematical expressions that are derived from a basic heterogeneous reaction theory. At a fixed furnace temperature, solid state kinetics type runs give proportionate values of reaction heat, reaction temperature, and thermal transfer and conductivity. At a linear programmed furnace temperature, TGA type runs give reaction heat and thermal coefficient values, while DTA–DSC type runs give reaction heat and temperature. These thermodynamic and physical parameters alone control the decomposition. By uniform agreement, the experimental conditions may be relaxed to give universally reproducible results. The exact conditions are specified for gravimetric and thermal calorimetry, and the required relaxation agreements stated for precisely reproducible results. Illustrations of analyzable gravimetric calorimetry are given for decompositions of $CaCO_3$ and $BaCl_2 \cdot H_2O$.

INTRODUCTION

The observation of the decomposition of a solid while the solid is being heated is invariably the observation of the conversion kinetics of a heterogeneous reaction. It is therefore essential to use the correct mathematical equations for heterogeneous decompositions to analyze the experimental data. A proper equation will give not only an analysis of the data but also will define the experimental conditions so that results will always be identical, that is, reproducible. Analyzable data can thus be reproduced, but a proper equation must show how only reproducible data may be readily obtained. Analyzable data and reproducible data are thus distinguishable, and, according to a new heterogeneous reaction theory[1], both can be achieved.

In the numerous studies on the analysis of thermal methods data, no fully successful technique has been reported. Among others, Sestak[2] and Flynn and Wall[3]

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have summarized the many methods proposed for the interpretation of TGA data, and Reed *et al.*[4] reviewed DTA–DSC analysis methods. Garn[5] has surveyed the entire field of thermal analysis.

Thermal analysis has come to mean observations at a linearly increasing temperature, but there is another equivalent thermal method. It is carried out with the furnace temperature fixed, and the results are called solid state kinetics studies. Young[6] among others has collected the numerous equations suggested for data analysis of fixed furnace temperature experiments. Again, none are fully successful.

The existence of the many inadequate interpretations for both fixed and linearly programmed temperature data indicates the lack of the proper mathematical analysis. Actually, all previous fixed and programmed furnace temperature experiments have not been carried out with the proper control of experimental conditions because no completely correct theory has been advanced. Meaningful analysis was impossible. Here, the mathematical equations from a proper heterogeneous reaction analysis[1] are presented. They show the experimental conditions which must be rigidly controlled to obtain exactly analyzable results. Further, they dictate how a restricted relaxation of these conditions in a manner requiring a universal agreement will give precisely reproducible results. These conditions are fully described and their experimental use demonstrated.

IDENTIFICATION OF EXPERIMENTAL METHODS

First, it is necessary to identify the types of experimental procedures employed for the thermal analysis of solids. Several are presently used. The major division occurs on the basis of the furnace temperature during the observation. Both fixed furnace temperature (FFT) and programmed furnace temperature (PFT) techniques are used.

In FFT experiments, the weight loss is normally followed. The results are generally identified as solid state kinetics studies.

With PFT experiments, a further division of techniques occurs. When a linear heating rate is used and the weight loss is followed, the method is called thermogravimetric analysis (TGA). When a linear heating rate is used and the difference in temperature between the furnace or a reference and some point in the sample is monitored, the method is designated differential thermal analysis (DTA); if the difference is used to control the process, it is called differential scanning calorimetry (DSC). These latter two aptly named differential methods, DTA and DSC, are essentially identical, being merely different temperature difference methods. As a group, the results of linearly programmed PFT techniques are generally identified as thermal methods of analysis.

Thermal methods actually include both FFT and PFT experiments, for whether a fixed or programmed furnace is used the result is basically the same. The reactant responds to thermal stress in both cases. Its reaction details in the conversion variable, time, will depend upon how the stress is delivered and how the conditions in the reactant control its acceptance. Both FFT and PFT processes are identical, differing only in the time scale of reactant to product conversion. The proper reactant variables must be identified, and their interaction with the system conditions expressed in suitable time-dependent mathematical equations. With the proper functions expressed in the correct independent variables, the FFT and PFT experiments can be properly designed for exact analyzability or precise reproducibility.

EQUATIONS FOR SIMPLE ENDOTHERMIC SOLID STATE DECOMPOSITIONS

On the basis of a new heterogeneous reaction theory[1], equations have been developed for simple endothermic solid state decomposition reactions. Such reactions include polymorphic solid state inversions, sublimations, solid state decompositions with all gaseous products, and solid state decompositions with at least one solid and one gaseous product which can reform the original reactant under suitable experimental conditions. Although the theory is quite general, the emphasis here will be limited to such endothermic reactions.

The theory may be briefly summarized. In essence, it recognizes that heterogeneous reactions take place only at the condition $\Delta G = 0$. All existent substances have a positive ΔG with respect to reaction, and, when they are stressed so that the ΔG should become negative, they respond by reacting at the zero ΔG-value. For a solid decomposed by heating, the decomposition corresponds to the conversion of the heat of reaction, ΔH, into entropy, ΔS, at the reaction temperature, T_R. The theory may be applied in terms of reactant-product variables, thermodynamics and system conditions to obtain a proper conversion-kinetics equation.

For a decomposing solid, the reaction heat from a furnace necessarily at a temperature in excess of T_R is accepted by the sample surface nearest the energy supply, at a constant T_R dictated by the system conditions. The solid state reaction is thus initiated when the furnace temperature, T_F, just exceeds the reaction temperature. Subsequently, the conversion progress is determined by the sample properties and the system behavior.

If the sample is a macroscopic solid, not a powder, and is pure, so that the material cannot get above its T_R but instead must react, a reaction interface is generated within the sample at the point where the zero ΔG condition occurs. This reaction interface moves through the sample in a fashion dictated by geometry and temperature–heat flow restraints. As the heat of reaction is usually much greater than the heat required to warm the product toward T_F, steady state heat transfer and/or heat flow conditions will be established between the furnace, the product layer forming around the reactant, and the reactant, assuming all of the heat entering the solid ultimately goes to reaction. Diffusion of a gaseous product out of the sample will never be the conversion limiting step, as heat flow in solids is much slower than gas diffusion. The conversion will thus proceed in accordance with a geometry-heat balance.

A heterogeneous conversion such as a solid state decomposition reaction can be effected with the reaction temperature constant or varying. What is important is that the variation or non-variation be known, so that a constant or variable value of T_R can be accommodated in the mathematical description of the process as the conversion proceeds in time. A fixed T_R simplifies the conversion description. If the reaction temperature is allowed to vary, a three-parameter equation — in time, temperature, and position — must be used to express the conversion rate. It is not impossible to solve such a problem, but a relatively simple solution is obtained if the constant T_R condition is maintained.

It is a solution which can be expressed in simple mathematical form. Not only is the heat of reaction which must be delivered to the reactant at the reaction interface then a literal constant, but also it travels across a steady state gradient to a constant reaction temperature. To keep the value of T_R constant throughout an entire reaction, the reaction conditions at the interface must be held constant during the conversion. This can be achieved by keeping the pressure of the decomposition gas at a constant value.

If the decomposition gas pressure is held constant, the zero free energy condition is fixed in association with one temperature. Should the pressure deviate, both the magnitude of the heat of reaction and the steady state heat flow rate will change during reaction. A heat flow rate to one fixed limit is preferable, since the geometry of the sample controls the form of the ultimate equations. Geometry enters the conversion as the basic dependent variable, not only describing the gradient but also defining the amount of the sample which has reacted.

One more geometrical condition must also be met. Heat flows in three dimensions. To ensure that all the heat entering the sample follows identical paths to the reaction interface, so that the mathematical descriptions of the conversion rate will be correct, the sample must have a macroscopic spherical shape. This requirement introduces into FFT or PFT studies an unusual experimental difficulty, but it can be met with some degree of satisfaction. In other words, solid spherical samples must be used. A preliminary study[7] on samples of supposed one-dimensional shape and of cylinders insulated at the ends showed that they are not satisfactory for conversion-rate analysis. To get thermal data analyzable by simple equations derived from steady state heat flow and reactant consumption, the spherical sample condition is required.

With all the prior conditions regarded as experimental necessities that must be met, the conversion of a solid decomposed under these rigid conditions will follow the equations previously derived for them[1]. For the various simple endothermic solid state decompositions of spherical samples, these are:

FFT, no solid product:

$$1-(1-\phi)^{\frac{1}{3}} = \frac{4\pi r_0^2 M h (T_F - T_R)}{g_0 \Delta H_{T_R}} t \tag{1}$$

FFT, one or more solid product:

$$1-(1-\phi)^{\frac{2}{3}} + \frac{2}{3}\left(\frac{\kappa - h r_0}{h r_0}\right) = \frac{8\pi r_0 M \kappa (T_F - T_R)}{3 g_0 \Delta H_{T_R}} t \tag{2}$$

PFT, no solid product:

$$1-(1-\phi)^{\frac{1}{3}} = \frac{2\pi r_0^2 M h\beta}{g_0 \Delta H_{T_R}} t^2 \tag{3}$$

PFT, one or more solid product:

$$1-(1-\phi)^{\frac{2}{3}} + \frac{2}{3}\left(\frac{\kappa - hr_0}{hr_0}\right) = \frac{4\pi r_0 M\kappa\beta}{3 g_0 \Delta H_{T_R}} t^2 \tag{4}$$

The symbols used in all these equations are defined as follows: ϕ, fraction reacted; h, heat transfer coefficient from the furnace atmosphere to the sample surface, in cal/cm^2. min.°C; κ, effective isotropic thermal conductivity of the product, in cal/cm. min. °C; r_0, the initial radius of the spherical sample; T_F, the furnace temperature; T_R, the reaction temperature; β, the linear heating rate in °C/min; ΔH, the heat of reaction at T_R, in cal/mole; M, the molecular weight of the reactant; g_o, the initial weight of the sample in grams; and t, the time in minutes.

All these equations represent reactant to product conversion. They are basically integrated rate expressions, somewhat similar to those for homogeneous reactions, in the form

$$f(\phi) = \chi t \quad (\text{or } \chi t^2) \tag{5}$$

where χ is the specific conversion constant identifiable in each equation as the constant coefficient of the time term. However, the specific conversion constants are directly calculable from reaction conditions. They are not specific rate constants, are not temperature dependent and have no activation energy. This is a characteristic of all heterogeneous processes. The variation of the specific conversion constants will be seen to be with the temperature difference, ΔT (or β for linear PFT runs). To increase the rate of a heterogeneous conversion, it is only necessary to change the ΔT driving the reaction.

To analyze a reaction and confirm that it obeys one of these equations, a plot of the left-hand function against t or t^2 is made. Where a numerical coefficient modifies the second member of this function, it is a correction that must be found by estimation. If the final plot is in linear form, the equation expresses the reaction behavior, as controlled by the physical parameters h and κ and by the thermodynamic constants T_R and ΔH. The values of these parameters control the correction and the slope of the line, and so permit a physical-thermodynamic characterization of the reaction from the thermal analysis.

The reaction proceeds after initiation only in time, since all the controlled conditions keep the possible variables constant. Time is the key variable. The custom in TGA and DTA–DSC of identifying the progress of a solid state conversion in terms of the normal abscissa variable, the temperature, is somewhat misleading. It is time which is varying after the reaction has begun. Although the temperature in terms of the heating rate does reflect time change, an identification of the peak temperature for a DTA–DSC curve is meaningless, for no indication of time is given in such a number.

In fact, DTA and DSC represent only part of the Eqns. (1)–(4) because of their differential nature. The temperature difference is the portion of the equations to which they are proportional. As such, they can give no information about conversion rates directly, merely showing by detecting one temperature in the reacting sample that it is consuming heat. The heat flow is of course under steady state conditions. Such calculations as those by Akita and Kase[8], and Melling *et al.*[9], are entirely erroneous, being based on unsteady heat flow equations. Further, the correlation of DTA data and rate are meaningless as the measurement is only differential. There is no degeneracy in the fraction reacted–heat flow geometry in a differential method, and conversion rates cannot be computed.

The fractional rate of conversion, $d\phi/dt$, can be found for the FFT or linear program PFT weight loss experiment, since weight loss affords an integral method of following the reaction. It is only necessary to differentiate the appropriate equation. Substitution will then give a numeric rate value, for spherical samples. Eqns. (1)–(4), it should be reiterated, apply only to spheres. With a computer and a function relating heat accumulation, heat flow and geometry, reaction conversion equations can be developed for other sample shapes. The spherical samples and their correspondent equations are just a readily testable situation for analyzability.

An examination of the equations and the conditions of their derivation clarifies one aspect of FFT experiments. It is assumed that the sample is everywhere close to its reaction temperature when the reaction is initiated. In solid state kinetics studies, the sample is normally inserted cold into a hot furnace. There are two consequences. The first is an induction period, occurring while the exterior of the sample warms to reaction temperature, leaving the interior still cool as only unsteady state heat flow has warmed it. The second is the acceleratory period, occurring as the exterior stays at reaction temperature for a relatively long period and contests with the cool interior for heat. A partition of heat results, with a decreasing amount going to the inside as the reaction progresses and an increasing amount going to the reaction; the warming of the interior of the sample to reaction temperature takes less and less heat as time progresses. An acceleratory effect on the reaction is observed. Neither the induction nor the acceleratory periods are real, being only artifacts of the experimental procedure.

Conventional TGA data, obtained with no provision to bring the entire sample to T_R before the run, is also colored with acceleratory effects. By rigid adherence to the conditions for which the Eqns. (1)–(4) apply, both FFT and linear PFT methods can be exact.

There is one apparent advantage in carrying out reactions by the PFT technique. In the retained product FFT equation, Eqn. (2), there are four unknown parameters, h, κ, T_R, and ΔH. However, in the linear PFT equation, Eqn. (4), only three appear, h, κ, and ΔH, as the known heating rate, β, replaces the temperature difference. The advantage is slight, as the mathematical properties of these equations limit the solutions of two runs solved simultaneously to ratios of the controlling parameters. Explicit values do of course come from the application of the equations.

The use of the equations in treating thermal data that is precisely analyzable under the different experimental regimes is described in the following section. Subsequently, the relaxation of the rigid controls is presented to show how exactly reproducible data can be observed.

ANALYZABLE THERMAL ANALYSES

To obtain thermal analysis data that are precisely analyzable, the run must be carried out under conditions which exactly and continuously adhere to those assumed to derive Eqns. (1)–(4). If this is done, the result is analyzable, that is, can be linearized when plotted according to the appropriated mathematical function, or, more significantly, can be precomputed from a knowledge of the system parameters. The major consequence of the rigorous conditions is experimental data to test the validity and reliability of the theoretical equations.

TABLE I

CONDITIONS FOR TAKING ANALYZABLE DATA BY THERMAL METHODS

Variable	*Gravimetric calorimetry*		*Thermal calorimetry*
	FFT *Solid state kinetics*	*PFT (linear)*	
		TGA	*DTA–DSC*
Material	Known	Known	Known
Purity	100%	100%	100%
Sample size	Any	Any	Any
Sample shape, macroscopic	Sphere	Sphere	Any
Sample type	Solid^a	Solid^a	Solid or powder
Sample encapsulation	Must be prevented	Must be prevented	Must be prevented
System volume	Any	Any	Any
System atmosphere pressure, decomposition gas	Constant^b	Constant^b	Constant^b
Pressure, inert gas	Zero^c	Zero^c	Zero^c
Initial temperature, sample	Just below T_R	Just below T_R	Just below T_R
Pre-heat	Essential	Essential	Essential

[a] Free-flowing powder samples cannot be used but must first be compacted into spherical shape. [b] May be any value but held constant during a run; composition need not be known; one convenient way[14] to achieve this is to evacuate the system and then decompose some of the sample in another part of the system, leaking pressure in excess of the constant level before and during the run. Also, a separate fixed temperature source of the sample connected to the system can serve both as a pressure supply and as a sink to maintain constant pressure. [c] A constant pressure may actually be used; a few systems or apparatus can be arranged to keep decomposition and inert gas pressures constant.

The experimental conditions to obtain analyzable data are listed in Table I. They can be met by appropriate system design. For instance, the decomposition gas pressure must be kept constant throughout the run; a pressure regulating device must therefore be incorporated in the apparatus. It is convenient if a pressure measuring device is also present, so that duplicate conditions of pressure can be set in subsequent comparative runs. This and the other pertinent conditions may be considered in connection with each technique.

FFT–gravimetric calorimetry: solid-state kinetics studies

A known material of 100% purity must be made into a sphere of any size, studied in a system of any volume in which the gas pressure can be controlled. Before the run is started, the sample must be pre-heated to near the reaction temperature of the conditions which will exist during the run. This step creates a simple heat flow during the run and eliminates the artificial induction and acceleratory periods characteristically observed in solid state kinetic studies[6].

A most effective way to accomplish this is to heat the sample for an extended period at a pressure well in excess of that to be employed during the run. The furnace can then be at its temperature during the preheating. To initiate the run, the pressure is suddenly reduced. Hills[10] used this method most effectively in studying calcite decomposition.

Maintaining all the conditions rigidly corresponds to the assumptions made in deriving Eqns. (1)–(4), so that they accurately represent the observed data. From the decomposition curve, characterizing values proportional to the physical and thermodynamic parameters controlling the particular decomposition can be evaluated.

PFT–gravimetric calorimetry: TGA

Exactly the same control over the experimental variables must be used for TGA as for the just described solid-state kinetics studies. The only deviation in procedure now required is a program interruption as the reaction temperature is approached. The sample is then allowed to sit for an extended period until it is near reaction temperature throughout before the actual run is made.

TGA possesses one inherent advantage over the FFT method. For the FFT technique, a value of the unknown T_R must be known. For TGA, on the other hand, the temperature difference is replaced by the known heating rate, β. It is still essential though, to have some idea of T_R so that a meaningful pre-heating period can be inserted into the thermal program. The actual merits of the one less parameter in the PFT method will be discussed later.

Either method gives values proportional to the physical parameters of the system. Both permit reduction of the observed data to linear form or of total prediction of the curve. Neither give any conventional homogeneous kinetics data. Since a solid state decomposition is a heterogeneous reaction, classical kinetics are lost. Conversion constants for a given set of conditions can be found, however, and they may be altered at will, consistent with the parameters appearing in the equations. As these parameters are physical and thermodynamic properties of the substance, methods following a reaction by weight loss are thus most aptly called gravimetric calorimetry.

PFT–thermal calorimetry: DTA–DSC

Since the equivalent DTA and DSC methods are differential sensing of heterogeneous reactions, the conditions under which their results may be analyzable differ from the total measurement type afforded by weight loss methods. These conditions are also listed in Table I. To discuss these, it is first necessary to restate carefully which parameters can be extracted from the differential methods.

First, a heterogeneous reaction is being studied. Second, the reaction is being followed by sensing a temperature difference existing within the reacting sample. This is only one of the factors controlling the conversion of the solid to its products, namely the ΔT. Because of this limitation, no conversion kinetics can be deduced. What the differential methods do afford is a very precise measure of two of the conversion parameters. These are the reaction temperature and the reaction heat.

To detect these accurately, the same conditions as in the previous two cases must be met. The material being examined needs to be a known substance so that suitable pre-heating can be introduced. To get the unique reaction temperature of a pure substance, the sample must contain 100% of that material; when the sample is not pure, the first break corresponds to the reaction of that substance in the presence of the specific impurities in that sample.

The reaction temperature is readily observed in DSC whether the sample is preheated or not, since the thermocouple is on the exterior of the sample. Another method, thermomechanical analysis (TMA), recently described by Miller *et al.*[11], also affords a sensitive measure of T_R without the necessity of preheating the sample. In DTA, though, a pre-heat period is needed to establish the true value of the reaction temperature.

For the DSC type observation, the pre-heat allows the magnitude of the reaction heat to be measured accurately. No effect of heat partition during the initial stages will disturb the deflection of the curve, and it will be almost linear in departure from the baseline. If the calibration standard was also treated in the same manner, a ΔH value much enhanced in accuracy is obtained.

Other conditions listed in Table I which differ from the gravimetric calorimetry case are the sample shape and form. Since conversion kinetics cannot be obtained from DTA or DSC (they might be with elaborate heat flow-geometry compensation design), the sample may take any form or type, even a powder. Detecting the temperature of the break from the baseline and the area of the total curve is not dependent on the actual shape, type or form of the sample. Other than this difference, all the other conditions are the same.

When these conditions are met, the differential methods give accurate values of the parameters they can observe. No general equations can be written for these methods; special equations might describe them if the heat flow pattern is uniquely correspondent to the geometry. In practice, because of the limited information available from an analyzable DTA or DSC run, it is not practicable. The differential methods give good calorimetric data, performing well as thermal calorimetry.

All of the stringent conditions needed for analyzability need not be met in practice. Their selective relaxation does destroy the unique analyzability but it can also lead to a highly useful reproducibility.

REPRODUCIBLE THERMAL ANALYSES

Reproducible data obtained by thermal analysis techniques are those which may be duplicated over and over. Such data need not necessarily be analyzable. With reproducibility the only requirement, a requirement which will permit identification by comparing a curve to a spectrum of predetermined curves measured at specified conditions, the thermal analysis procedure may be carried out under less rigorous controls than those required for analyzable data.

The specified conditions can thus be any selected convenient set, chosen either internationally or within one laboratory on the basis of operational ease but which are consistent with the variables entering Eqns. (1)–(4). Duplicate observation is the only goal. To have reproducibility, then, conditions need not be rigidly correspondent with those needed for mathematical analysis. But in selecting the universally acceptable experiment, the proper variables must be recognized as the parameters controlling the observed results.

For instance, pre-heating was essential in obtaining analyzable data. It need not be carried out. However, the resultant data will reflect the artificial acceleration period due to the initial partition of heat occurring during the initial stages of the decomposition in either a FFT or PFT observation. If the same fixed furnace temperature and the same initially cold temperature of the sample are always employed in FFT runs, or if the same heating rate is employed in PFT runs, the curves will correspond to no simple mathematical expression, but they will be the same. In other words, any furnace temperature–sample temperature relation may be used, provided it is always the same.

The sample geometry, by the same token, must also be the same. Again, there is no need for it to be spherical — only a need for it to always be identical in every experiment carried out anywhere. Perhaps the most readily duplicable sample shape is a cylinder, made to a preselected length in a pellet press and with the same pressure; its gross shape and weight must always be the same. Such conditions can be met, but they must be decided upon.

What is important in generating the identical curve in every measurement then is the same factors that lead to the mathematical expressions of Eqns. (1)–(4). Whether the sample is pre-heated or not is not important; it is only important that it is always heated during the experiment in the same manner. Whether the sample is spherical or not is not important; it is only important that it is always an exact duplicate.

Likewise, the pressure was carefully controlled to get analyzable data, to keep T_R constant and eliminate variation in ΔH_{T_R}. This is not necessary merely for reproducibility. But if the pressure of the decomposition gas during the thermal analysis is permitted to vary, it must be made to vary precisely the same way every time.

Reproducible data, in short, need not be taken under any mathematically limiting conditions but only under conditions chosen for utility in such a way that they are consistent with the mathematical variables influencing the run. Then, everyone must do thermal analysis in that same fashion using identical systems. The result will be data highly successful in identifying the solid material. No values of the parameters can be extracted, but precise analytical identification will be possible by all.

The minimum conditions which are either inviolate and must be met or which must be settled by cooperative choice can best be summarized in connection with each type experiment. These are listed in Table II. Some comments are appropriate for each experimental technique.

TABLE II

CONDITIONS FOR TAKING REPRODUCIBLE DATA BY THERMAL METHODS

Variable	*FFT Solid state kinetics*	*PFT (linear)*	
		TGA	*DTA-DSC*
Material	Unknown[a]	Unknown	Unknown
Purity	Any	Any	Any
Sample size	Pre-agreed[b]	Pre-agreed[b]	Pre-agreed[b]
Sample shape, macroscopic	Pre-agreed	Pre-agreed	Pre-agreed
Sample type	Any	Any	Any
If powder type, cup size and shape, sample particle size and distribution	Pre-agreed	Pre-agreed	Pre-agreed
If powder type, particle packing	Identical[c]	Identical[c]	Identical[c]
Sample encapsulation	Pre-agreed manner	Pre-agreed manner	Pre-agreed manner
System volume	Same for all instruments	Same for all instruments	Same for all instruments
System atmosphere pressure decomposition gas pressure, inert gas	May vary; variation must be pre-agreed	May vary; variation must be pre-agreed	May vary; variation must be pre-agreed
Initial temperature, sample	Any; must be pre-agreed	Any; must be pre-agreed	Any; must be pre-agreed
Pre-heat	None	None	None

[a] Because unknown materials are usually being examined, FFT methods are of little utility. The lack of basis for furnace temperature choice destroys their flexibility. PFT methods are flexible. If in FFT methods the sample identity is known, the remaining conditions are needed. [b] All entries of "Pre-agreed" require universal agreement for the development and use of an absolutely general catalogue of curves. [c] Exact packing duplication is the biggest problem in reproducibility.

FFT: solid state kinetics studies by weight loss

This is the least useful technique for reproducibility. Its disadvantage is simple. Since the material being studied for identification is presumably unknown, there is no easy way to preselect a suitable furnace temperature for the experiment. If the temperature is too high, the result is almost instant weight loss, destroying any identifying wave and reducing the measurement to a classic weight loss analysis. If the temperature is too low, no decomposition occurs.

On a routine basis where some knowledge of the sample constituents exists, it would be possible to set a furnace temperature. It would not be convenient though, to have a universal catalogue of identifying curves. The conditions listed in Table II for this type experiment are of course capable of being selected, but only for small scale usage. Programmed methods seem much superior.

PFT:TGA

There is no limitation on the use of this method, since the entire range of temperatures can be scanned with an unknown material. Scanning the entire range introduces a time factor, and it may predicate choosing a relatively rapid scanning rate. With a rapid rate two reactions can be merged, such as the loss of the first and second waters of hydration from a hydrate, normally separable at a slow rate. A judicious choice must be exercised in such cases, and the ultimate universal selection may lead to a catalogue of TGA data taken at two heating rates, one fast and one slow.

The most severe limit to reproducible data by TGA (or by any thermal method, FFT or PFT) is introduced if the sample is in powdered form. Powders permit unsteady state heat flow through voids and do not form duplicate geometrical samples, even on successive runs in the same apparatus. By sieving between two selected sieve sizes, a sample with a fairly narrow cut particle size can be obtained, and in such a case the particle size distribution will be reasonably alike for all samples. Forming the sample itself is the real problem. First, an agreement would be required on the sample cup shape and size. But getting the sample of the same mass into identical packings twice is literally impossible. It could be done within limits, and for samples containing only one material the TGA curves would be highly characteristic. For samples containing a mixture of materials, though, there might be overlap of the now reduced decomposition steps, particularly at rapid heating rates.

All the factors in the selection of cup and sample size require careful consideration if the convenience of powders leads to their standard use. There is of course no limit on the size of the sample, but a large sample requires a considerable period of time for the reaction heat to be supplied. Decomposition step overlaps become more readily possible. This favors the use of less massive samples, which in turn magnifies the irregularities in packed powder samples. Some compromise in choice will have to be made.

Beyond these points, the other conditions listed in Table II for TGA must be selected. Once they are, then the reproducible technique can be used on a universal scale for identification of materials, its only use.

PFT: DTA–DSC

The discussion immediately preceeding on the inherent difficulties of using powdered samples applies equally to this thermal analysis technique. It is even more significant here, since only two temperatures within the decomposing sample are monitored. The differential measurement is made in only one geometric plane, and powder irregularities can easily distort the contents of that plane.

DTA is the technique most susceptible to this fault. It requires burying the thermocouple within the sample, a requirement met most easily with powders. Since a cylindrical cup is normally used, the measurement is actually in the plane through the interior thermocouple junction. Any slight geometric content variations in this plane dramatically influence the shape of the observed thermogram. A sufficiently large sample diameter will help minimize irregularities through statistical effects.

As DSC employs an external thermocouple, the sample need not be a powder. But with a solid sample resting on the hot sample cup difficulties may arise if decomposition gas must exit too rapidly. Since only an identical procedure is required, whatever changes occur must always be duplicated. Perhaps the best way to employ the DSC technique is to use a small sample, for this minimizes the effects of any variation in the reaction conditions and at the same time separates responses in the thermal spectrum most efficiently.

The small sample is useful with DSC for another reason. The thermocouple is external to the sample, in the face of the cup-furnace. As such, it is really measuring the temperature of the surface plane of the cup normal to heat flow. The cup is usually constructed of metal, and with the high thermal conductivity of metal any temperature variation in the surface of the cup-furnace is sensed at any spot on the surface. The technique is thus less sensitive to sample irregularities. In fact, a quite suitable choice of standard sample might be 25 grains of powder, meshed to between 140–160 mesh size and spread in a single layer over the sample pan. The metal conductance permits sensing a reduced temperature anywhere on the surface of the sample holder. The temperature difference will of course be small, but with the detection sensors and sophisticated electronics now incorporated in thermal instruments, any deviation can be measured and amplified.

With the external thermocouple, a DSC reproducible run affords a good measure of one of the reaction parameters, the reaction temperature. As the furnace and the sample surface are the same temperature prior to reaction, the first deviation from the baseline is a precise measure of the reaction temperature under the conditions existing in the system. DTA does not afford this in reproducible runs, for the central temperature in the sample is not yet the reaction temperature. Preheating, used in the analyzable case, does make the temperature registered on the output from DTA the reaction temperature. But for DSC no pre-heating is needed. The DSC reproducible run is very close to the analyzable run in this measurement.

The same thing is true for the other parameter which can be measured by DTA or DSC, the reaction heat. Since this is done *via* calibration, a calibration which included a matched variation of conditions would automatically permit the conversion of the area of the curve into close to the actual value of ΔH. The major limitation to this is the fact that the pressure is allowed to vary, thus varying T_R and consequently ΔH. Of course, if the reaction heat is not a sensitive function of the temperature, this error may well be tolerable.

Whether the reaction temperature and heat can be determined from a DTA or DSC run in no way affects the reproducible character of the curve. Quite successfully, if it is taken under a set of pre-accepted conditions, it can be used for identification.

All the techniques may thus be used generally, either for analytical identification through reproducible data or for accurate gravimetric or thermal calorimetric data from which conversion rates and physical parameters may be extracted. The detailed use of both types needs to be considered next.

THERMAL METHODS IN USE

Within the limits described for each of the FFT and PFT methods, thermal analysis offers a distinctly unique way to characterize an endothermic solid state decomposition reaction. Following the weight loss during reaction gives heterogeneous conversion rate data, product thermal properties and conversion thermodynamic data. In a DTA–DSC procedure, calibration allows the conversion thermodynamic data to be determined. Both the weight loss and differential techniques require severe experimental restraints to assure analyzable results and accurate data. On the other hand, if the restraints are relaxed, data useful for the identification of a material may be obtained, provided a pre-existing spectrum of decomposition curves has been obtained under exactly equivalent conditions so that reproducible results are compared.

The experimental conditions for universal reproducibility must be set by international agreement or, for limited special comparison, by agreement within an individual laboratory. Once this is done, it becomes routine to identify a substance and determine the amount of it present in a sample.

Although material identification can thus be made, no absolute conversion data will be obtained. To get absolute, mathematically analyzable data, a weight loss method and the more severe restraints must be used. A particular mathematical quirk limits the generality of the resultant data. Two runs at different conditions cannot be solved simultaneously to extract values of the conversion controlling parameters. The result with FFT runs is only ratios of the four parameters, h, κ, T_R, and ΔH. In PFT methods, the reaction temperature disappears as an explicit variable, but still only κ/h and $\kappa/\Delta H$ ratios result from the values of the linear correction and slope. The reliability of the theory is confirmed by the reduction of the data to linear form, but numeric values of the physical and thermodynamic parameters incorporated in Eqns. (1)–(4) cannot be obtained directly.

If a value of one of the parameters is known, the others can be found. Heat of reaction values determined in a calorimeter can be corrected down to the T_R fixed by the zero free energy change by means of ΔC_P data. With the proper ΔH value, h and κ values may be computed from the data of a single experiment. This is a relatively uninteresting exercise to the chemist. Reaction heat values themselves, particularly for the decomposition of pure materials not previously investigated, are of far greater interest.

One way to obtain reaction heat values from a single run is to precompute h for a given furnace atmosphere at a particular temperature or temperature regime by standard engineering methods. Another way is to calibrate the h-values for a series of furnace conditions with a reaction whose ΔH is precisely known at the conditions.

As the heat transfer coefficient depends principally on gas pressure, it is the most accessible parameter. When it is known, the heat of reaction may be evaluated from a single, analyzable FFT of linear PFT–TGA experiment by the use of the integrated conversion equations.

It is important to restate that conventional homogeneous kinetics parameters cannot be extracted from either a FFT or PFT decomposition study, since conventional kinetics are not observable in decomposition reactions. They are heterogeneous reactions, and the conversion obeys equations of the type used here. Thus, only the physical and thermodynamic parameters are observed. Much better names for the analyzable FFT and PFT experiments may be based on this property. Any weight loss method, carried out in analyzable fashion either as a FFT or linear PFT experiment, affords a full knowledge of the decomposition reaction thermodynamics. It is thus more appropriately called gravimetric calorimetry.

Similarly, analyzable DTA–DSC observations give *via* calibration accurate values of the reaction temperature and reaction heat. Although this method does not yield the other heterogeneous kinetics parameters, particularly since there is no way to convert DTA–DSC data into conversion rate information, the differential temperature method is an excellent measure of the thermodynamics or the reaction. It is thus more aptly called thermal calorimetry.

The two methods combined offer a unique and unusual form for rapid and precise calorimetry, in many ways superior to a conventional calorimeter, as well as delineating the conversion kinetics. With DTA–DSC, a reaction heat value can be precisely found. If it is then employed in evaluating the parameters of an equivalent, analyzable linear PFT–TGA run (or FFT run, if that procedure is convenient), its accuracy can be established and the heterogeneous kinetics of the particular decomposition determined exactly.

Alone, the methods work equally well in measuring the parameters each can measure. Gravimetric calorimetry inherently contains more information in its experimental results. To illustrate its use, some heterogeneous decomposition reactions have been studied.

APPLICATIONS

To demonstrate the applicability of the equations of gravimetric calorimetry, two reactions were studied. Both are simple endothermic solid state decompositions with a gaseous product. One reactant was a hydrate, the other a carbonate. For these studies, the reaction conditions were rigorously controlled so the results would be fully analyzable. Each reaction will be described individually.

Barium chloride monohydrate decomposition

The thermal decomposition of $BaCl_2 \cdot H_2O$ was carried out using linear PFT methods only. In the system available it is inconvenient to have a water vapor in excess of a few millimeters without inducing condensation in the system. This limit imposed by the room temperature prevents making satisfactory FFT runs.

For the study, Baker's Analyzed Reagent Grade barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) was ground and used to form hand-shaped spherical samples. The sphere was suspended in a cage formed of three wires from a Cahn RG Recording Balance housed in a glass vacuum system. The system was evacuated, and 10-mm water vapor pressure introduced, as measured by a manometer located between the Welch Vacuum Pump and the Cahn Balance housing. A Marshall furnace surrounded the sample in the hangdown tube. Holding the hangdown tube at 90°C overnight both changed the dihydrate to the monohydrate and pre-heated the sample prior to the initiation of the run.

The run was carried out at a heating rate of 1.0°/min. An F& M 240M Programmer sensing a T/C in the furnace controlled the rate. A stopcock across the measuring manometer was used to maintain the pressure at a constant value throughout the entire run. The weight loss was recorded on a Sargent SR Recorder, and the temperature of a T/C inside the hangdown tube was followed on a Moseley 2D-4 X-Y Recorder.

A plot of the observed data is shown in Fig. 1. The fraction reacted, ϕ, a symbol introduced to define the fraction converted in a heterogeneous reaction, is shown in this plot as a function of time. It will be seen that the curve is shaped like a typical TGA curve.

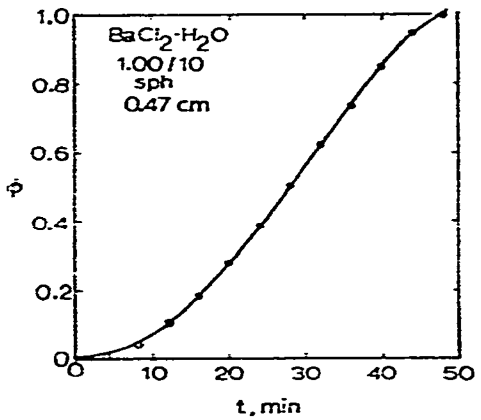

Fig. 1. Decomposition curve of barium chloride monohydrate observed by gravimetric calorimetry using a programed furnace temperature (TGA type). Initial curve break, the reaction temperature, 93°C; heating rate, 1.0°/min; pre-heating, overnight; diameter of spherical sample, 0.48 cm; sphere weight, 821 mg; constant water vapor pressure, 10 mm.

However, it can be readily analyzed. A straight line is obtained when the data are plotted according to Eqn. (4) with a correction of -0.20, far from the 2/3 limiting value, in the ϕ-function term. Fig. 2 is a plot of the $f(\phi)$ against t^2. Consistent values of h, κ, and ΔH are given with the figure. To compute ΔH in this demonstration case, reaction heat values at 298°K were corrected to the reaction temperature, 366°K, by heat capacity data[12]. The data are linear from 1–99%, indicating the validity of the solid state decomposition expression.

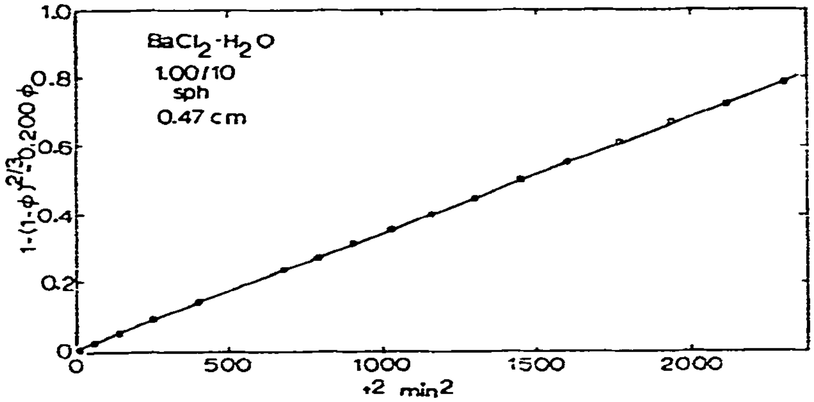

Fig. 2. The barium chloride monohydrate decomposition curve of Fig. 1 plotted according to Eqn. (4) of the text. The linearizing correction value is the coefficient of the second term of the ordinate. The straight line has a slope of 3.4×10^{-4} min^{-2}, consistent with values of h of 2.7×10^{-2} cal/cm^2. min.°C, κ of 9.0×10^{-3} cal/cm. min.°C, and ΔH of 15.0 kcal/mole.

Calcium carbonate decomposition

The thermal decomposition of $CaCO_3$ was carried out both by FFT and PFT techniques, to show that the correspondent equations were reliable for both methods. For both studies, Baker's Analyzed Reagent Grade $CaCO_3$ was ground and hand-fashioned into spherical samples which were suspended in three-wire cages.

FFT runs, $CaCO_3$. — For the FFT study, the sample was suspended from an indicating Mettler Balance into a flow-through hangdown tube mounted in a constant temperature furnace wound with Nichrome wire and controlled by a Tem-Press Regulator system. Pre-heating was achieved by placing the sample under 1-atm CO_2 pressure and heating the sample overnight to the selected temperature of the FFT run. To initiate the run, the atmosphere was changed to flowing nitrogen. This ingenious technique was developed by Hills[10] for a calcite decomposition study. His data, taken on spherical samples, are completely analyzable. A test[1] of it with the equations given here results in excellent linear plots.

However, four parameters occur in FFT analysis, all in ratio form. In an effort to determine the value of T_R under zero CO_2 pressure, an extensive study[13] of the calcite decomposition was made. Two of the results of this study are shown in Fig. 3, for runs at furnace temperatures of 987 and 1090°K. Curves consisting entirely of the typical decay curves of solid state kinetics studies are obtained, with no trace of the artificial induction or acceleratory periods. For reactions which can conveniently be exposed to high pressures of the decomposition gas product, this method offers a convenient FFT way to measure heterogeneous decomposition conversion kinetics.

Again, using Eqn. (2), the FFT form, the two curves of Fig. 3 become straight lines, as shown in Fig. 4. A correction of -0.62 is needed for the 987°K run and of -0.55 for the 1090°K one, reflecting the variation of h and κ with temperature. Values of h and κ may be computed if values of the non-indepedent ΔH and T_R are

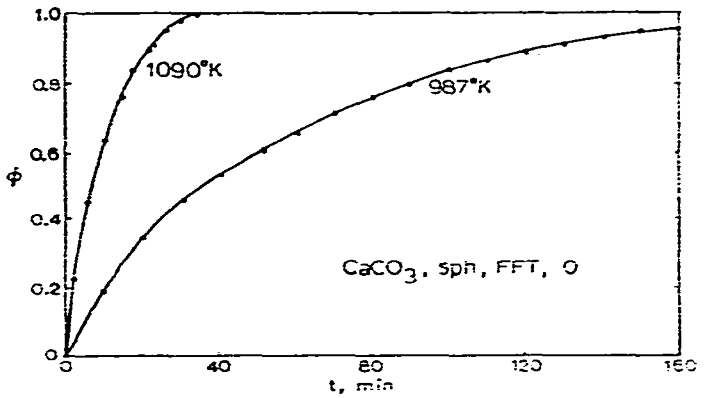

Fig. 3. Decomposition curves of calcium carbonate observed by gravimetric calorimetry using fixed furnace temperatures (solid state kinetics type). For 987°K run, sample weight, 429 mg, sphere radius, 0.45 cm; for 1090°K run, sample weight, 315 mg, sphere radius, 0.38 cm. Pre-heating period, overnight, at a pressure of one atm of carbon dioxide. Runs were carried out under one atm flowing nitrogen.

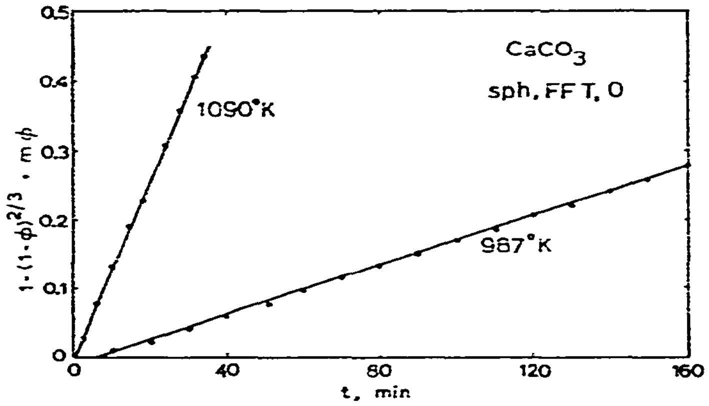

Fig. 4. The calcium carbonate decomposition curves of Fig. 3 plotted according to Eqn. (2) of the text. The linearizing correction value (the coefficient *m* of the second term of the ordinate) for the 987°K run is −0.62, for the 1090°K run, −0.55. For the 987°K straight line, the slope is 0.00187 min^{-1}, and for the 1090°K straight line, 0.0129 min^{-1}. Both slopes are consistent with a ΔH-value of 41.2 kcal/mole at a T_R of 773°K.

computed from the zero free energy change condition. One set of ΔH and T_R values are indicated with the figure, using the reaction heat at 298°K corrected by suitable heat capacity data[12]. Because of the four unknown parameters in FFT observations, and because FFT unlike PFT experiments give no indication of T_R, unique values of the four cannot be found from the data alone. It is a disadvantage of the FFT method that a numeric value of *h* must be known. However, the linear plot of the data does show that the equation validly describes the decomposition behaviour.

PFT runs, $CaCO_3$. — To confirm that calcite decomposes according to the similar equation in PFT experiments, equivalent samples of $CaCO_3$ were followed by TGA. The same Cahn Balance-Sargent Recorder system was used as in the

$BaCl_2 \cdot H_2O$ study. For this study, 10-mm CO_2 pressure was admitted to the sample chamber and the sample pre-heated at 730 °C overnight. The run was then made at a linear heating rate of 0.58°/min, with the pressure held constant during the run.

The observed data is plotted in Fig. 5, again showing the typical s-shaped curve associated with TGA. This curve is analyzable, as shown by the same data plotted in Fig. 6, according to Eqn. (4), the PFT form. The straight line results with a correction of -0.53 incorporated in the complex ϕ-function. From the correction and the slope, and from the T_R value observed, h, κ, and ΔH can be computed, as given with the figure. Again, the equation is a proper description of the decomposition reaction.

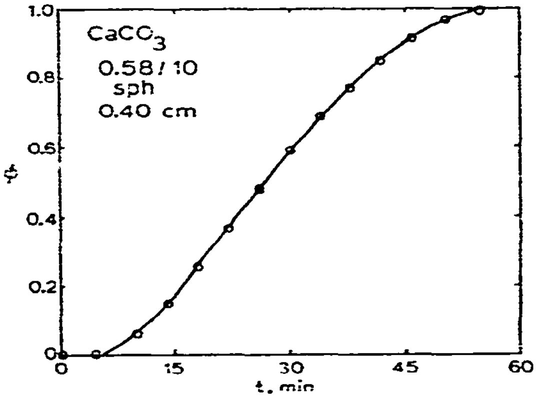

Fig. 5. Decomposition curve of calcium carbonate observed by gravimetric calorimetry using a programed furnace temperature (TGA type). Initial curve break, the reaction temperature, 737 °C; heating rate, 0.58 °/min; pre-heating, overnight; diameter of spherical sample, 0.40 cm; sphere weight, 329 mg; constant carbon dioxide pressure, 10 mm.

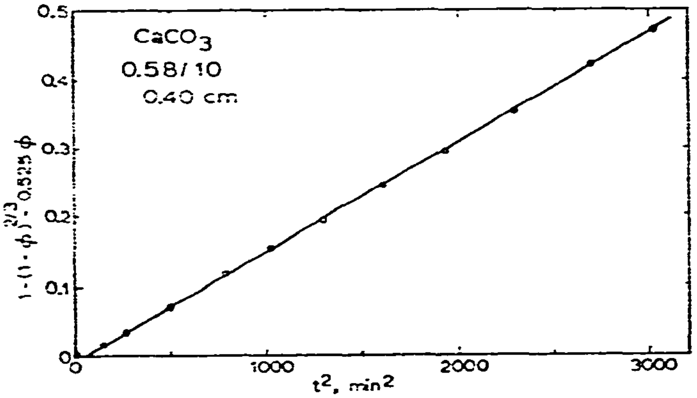

Fig. 6. The calcium carbonate decomposition curve of Fig. 5 plotted according to Eqn. (4) of the text. The linearizing correction value is the coefficient of the second term of the ordinate. The straight line has a slope of 1.6×10^{-4} min^{-2}, consistent with values of h of 3.8×10^{-2} cal/cm^2. min. °C, κ of 3.2×10^{-3} cal/cm. min. °C and ΔH of 40.0 kcal/mole.

Together, the total mathematical analysis of the hydrate and carbonate decompositions demonstrate that the theory reliably leads to valid equations. With appropriately calibrated systems, reaction heats may be determined accurately. Thus, for reactions which loose weight on decomposition, a proper TGA experiment behaves as a calorimeter. Gravimetric calorimetry is thus the more correct name for this linear PFT thermal method.

EXTENSIONS

All of the reactions treated here are simple, single-step endothermic heterogeneous decompositions. They are the easiest to analyze, for the conditions leading to the equations they rigorously obey are experimentally accessible. Usually, these reactions can be reversed. Work is now in progress to study reactions that cannot be reversed, such as the dehydration of hydroxides. Reactions of this type should follow the equations that have been presented, although some modifications may be dictated in the course of the work.

Unquestionably, the equations will be modified when the appropriate condition limits are invoked to derive the exact mathematical description of other thermally initiated heterogeneous reactions. Included in these are exothermic solid state decompositions, solid–solid reactions and adsorption. If the governing conditions are extended to include not only energy transfer but also mass transfer, exact equations can be developed for such reactions as corrosion, combustion, recombination, electrochemistry and crystal growth. Mixed reactions, those nominally homogeneous but affected or dominated by heterogeneous behavior, may also be properly described mathematically. Reactions of this type include unimolecular gas phase reactions, gaseous explosions, reactions studied by relaxation methods and catalysis.

On completing the development of the equations appropriate to describe the kinetics of every heterogeneous reaction, a full catalogue of analyzable conditions and the concomitant mathematical expressions will be available for use. Beyond the quantitative expression given decomposition reactions by thermal analysis here, it is an ultimate goal to extend the heterogeneous reaction theory to the suite of equations describing all such reactions.

CONCLUSIONS

For simple endothermic solid state decompositions, rigorous experimental conditions may be defined from a proper heterogeneous reaction theory so that precisely analyzable data can be obtained.

Relaxation of these conditions in a fashion agreed upon by those employing thermal methods will lead to universally reproducible data suitable for identification.

Equations consistent with the analyzable conditions fully describe the progress of decompositions followed by weight loss when carried out either at a fixed furnace temperature or at a linearly programmed furnace temperature.

The mathematical description of the reaction kinetics for data from analyzable weight loss measurements shows that the procedure is gravimetric calorimetry, giving conversion rate data, thermal parameters, reaction temperature and the heat of reaction.

Similarly, differential DTA–DSC methods, while yielding no rate data, are uniquely thermal calorimetry, giving only values of the reaction temperature and heat.

Gravimetric calorimetry applied to the decomposition of barium chloride monohydrate and calcium carbonate demonstrate its validity and precision.

The heterogeneous reaction theory used here to derive the mathematical expressions for gravimetric calorimetry is totally general and can be extended to provide a quantitative description of all heterogeneous reactions.

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