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Kinetic aspects of the thermal stability of ionic solids

Michael E. Brown[a,*], Richard E. Brown[b,1]

[a]Chemistry Department, Rhodes University, Grahamstown 6140, South Africa
[b]Department of Aerospace Engineering, University of Glasgow, Glasgow G12 8QQ, Scotland, UK

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Abstract

The kinetics of thermal decomposition of numerous ionic solids have been studied intensively for many years by chemists, physicists, materials scientists and chemical engineers. Many of the reactions studied form the basis of economically important industrial processes, for example, cement and ceramic production, catalyst manufacture, etc. In spite of all this effort, it is not possible to predict, from chemical knowledge and physical properties, what the thermal stability of a hitherto untested solid will be, or even to predict with certainty what the behaviour of a new sample of a well-tested substance will be.

Some of the kinetic trends and correlations that have been identified are reviewed and possible reasons for the lack of emergence of a theory capable of predicting thermal behaviour are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermal stability; Ionic solids; Kinetics; Thermal decomposition; Crystolysis

1. Introduction

Reasons for studying the thermal decompositions of solids (crystolysis [1]) may range from the very practical to the very theoretical. Examination of the thermal behaviour of a large number of different kinds of solid reactants under a variety of conditions has the ultimate goal of producing a theory of thermal stability of solids (TTSS). This paper will debate the possibility that this goal may be unattainable. Laidler [2] has pointed out that chemical kinetics was essentially an empirical subject until about 1900, after which the ideas of thermodynamics, the kinetic theory of gases and of molecular statistics began to be combined to explain elementary reactions. The development of the transition-state theory around 1935 by Eyring, Polanyi and Evans was a considerable improvement on collision theory and has led to qualitative insights into such features of homogeneous reactions as solvent effects, isotope effects and pressure influences. Shannon [3] has discussed applications of transition-state theory to the decompositions of solids.

The temperature dependences of rates of reactions of solids are often satisfactorily expressed by the Arrhenius equation, but the significance of the derived Arrhenius parameters (activation energy, E and pre-exponential factor, A) must be different to interpretations developed from the theories of homogeneous reactions [4].

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[*] Corresponding author. Tel.: +27-46-603-8254; fax: +27-46-622-5109.
E-mail addresses: m.brown@ru.ac.za (M.E. Brown), r.e.brown@ic.ac.uk (R.E. Brown)

[1] Current address: Department of Aeronautics, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK. Tel.: +44 (0) 171 594 5151; fax: +44 (0) 171 584 8120

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2. A theory of thermal stability

An acceptable theory, of any kind, should be able to explain a range of observations using fewer principles than there are observations. The theory should also be able to predict, with reliability, the behaviour of untested systems.

As the number of different experimental observations increases, the number of principles required to construct a satisfactory theory will also generally be forced to increase. There is a large body of information (rate equations, Arrhenius parameters, etc.) available on the thermal behaviour of a variety of well-characterised (i.e., particle sizes and distributions, defect and impurity contents, sample masses, prevailing gas pressures, etc.) samples of solid reactants (e.g., calcium carbonate) decomposed under various experimental conditions. From this body of information, could one expect to predict details (rate equation, Arrhenius parameters, etc.) of the thermal decomposition of an untested sample (of calcium carbonate) from measurements of some of these variables?

On an even wider level, if a lot of experimental information is available on the thermal decompositions of various chemically related reactants (e.g., metal carbonates except, say, barium carbonate, and also a lot of information on the thermal decompositions of various barium salts) could one successfully predict details of the thermal decomposition of an untested reactant (such as barium carbonate)?

One of the principles that is accepted as influencing thermal stability is crystal structure. Each crystalline substance has a unique structure. Those substances classified as isomorphous have overall similarities in symmetry, but unique dimensions, and single substances can take up different crystal structures under different conditions, for example, temperature, pressure, presence of impurities, etc. These structural and dimensional differences result in differences in lattice energies and other physical properties, such as thermal and electrical conductivities, etc. Even for one substance, with one crystal structure (maintained through a range of conditions), each preparation or sample of the substance will have a unique set and distribution of imperfections of various kinds, so that, in practice, no two samples of a solid can ever be identical, although they may be closely similar.

There are many indications that deviations from an ideal structure may have a greater influence on the thermal stability of some solids than the crystal structure itself, as shown by the differences in kinetic behaviour often observed between single crystals and powdered samples of the same reactant. Traces of impurities can also influence thermal stability without changing the crystal structure.

If the thermal behaviour of each crystalline substance counts for as little as one observation, can a small number of principles be used to interpret this large amount of information?

When comparing thermal stabilities of samples, the behaviour of similar single crystals of different reactants A, B and C, may show smaller variation than that found for reactant A (say) in sample forms $1, 2, \ldots, n$. Such observations suggest that a matrix of factors, in weighted combination, result in an observed thermal stability. Experimental variation of some of these factors, if such variations can be produced without changes in interrelated factors, may indicate whether the weighting factors are large or small. It appears extremely unlikely, however, that any single chemical step, such as the individual bond rupture or electron transfer steps proposed in homogeneous reaction mechanisms, can be unambiguously identified as rate controlling. Steps such as bond rupture or electron transfer in the solid state or on a solid surface will be influenced, at least to some extent, by the environment in which the process occurs and this environment is likely to change both with location and with time.

Reaction, localised at an interface, can hardly be significantly influenced by material remote from the interface [5]. However, in the absence of unreacted material, reaction will cease. The activated complex of homogeneous kinetic theory has to be modified to what we will call a reaction situation (RS). Reaction of an RS may produce more RSs. If the number and/or the reactivity increases, acceleratory behaviour results. Linear behaviour could result from constant numbers and reactivity, or increasing numbers of lower reactivity (or, in principle, decreasing numbers of increased reactivity). The rate of formation of new RSs will be related to the amount of ‘contactable’ unreacted material, which will probably be approximately represented by the overall unreacted material $(1-\alpha)$. A range of different reaction situations will be generated during the course of decomposition of a solid and here the work of Burnham et al. on the thermal behaviour of complex materials with distributed reactivity is important [6–9].

In experimental terms, decompositions are studied by low-resolution bulk measurements such as of changes in mass of a sample, or of accumulated pressure of gas evolved from the sample. Such measurements average out the detailed behaviour which occurs at the microscopic level. The microscopic behaviour can only be revealed, to some extent, by repeated measurements with altered sample histories. A very few experimental measurements have been performed on complex decompositions in such a way as to attempt to isolate all but a few of the experimental variables, or to measure and correlate the changes in a wider range of sample properties. An example of the former is the work by Powell and Searcy [10] who examined the evolution of gases in vacuum from selected crystal faces of carbonates.

The connectivity of factors [11] prevents complex systems from being understood by subdividing the system and examining a part separately, that is, no part of the system is representative of the system as a whole. The question of interest then might become: if the complex system is comprised of all the decompositions of all the solids possible, under a wide range of experimental conditions, can one usefully examine any subset and use the results obtained to explain and/or make general predictions about the complex system? (This is more-or-less equivalent to making predictions about world weather from observation of the weather in one selected geographical area?)

3. Formulation of the problem

Let the set *C* enumerate a sufficiently large sample of the chemical systems (individual samples of a range of inorganic solids) to which we hope to apply a theory of thermal stability. Assume that the systems in set *C* can be identified by the measured values of a set of *n* physical properties (such as chemical composition, crystal structure, sample mass, particle sizes and distributions, defect content, etc.) such that any system *A* (e.g., a particular sample of $CaCO_3$ with measured properties) in *C* can be represented as a point *P*(*A*) in an *n*-dimensional space of properties, *P* (Fig. 1). One possible set of co-ordinates for *P* can be constructed

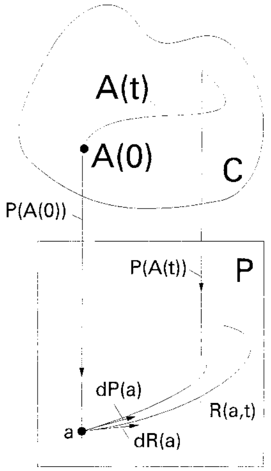

Fig. 1. Schematic showing a mapping of a reaction path onto property space, a theoretically derived reaction path and the associated rate equations as tangent vectors.

from the range of physically-realistic values of the physical properties of the chemical systems in *C*. The map $P: C\rightarrow P$ is equivalent to an idealisation by measurement of the physical world. We make no assumption that the measurement process is sufficiently discerning such that a chemical system in *C* can be uniquely determined by the values of its chemical properties. In other words the inverse map $P^{-1}: P\rightarrow C$ may not exist, For example, some information about the sample may have been measured, but not enough to specify it uniquely.

For any theory of thermal stability to yield a successful condensation of measured data, the dimension *n* of *P* should be much smaller than the number of systems in *C*, or, in other words, the values of some set of physical properties of the systems in *C* should form a more compact description of the systems than the enumerating system used to construct *C* itself. If this condensation is not possible, then the space *P* forms no more useful characterisation of the set *C* than *C* itself and we might as well consider a separate theory of thermal stability for each of the systems in *C*. One particular situation where this condensation may fail is where the number, type and position of atomic-scale defects, or other details of the specific microstructure of a given chemical system, are very critical in determining its thermal behaviour. In this situation the dimension of *P* could approach the order of the number of unit cells comprising the systems in *C*.

A thermal transformation of system A (where A is a member of C) yields a sequence of systems (all assumed to be also in C) $A(t)$, where t is a suitable parameter arranging the sequence of systems in order of their appearance as t is allowed to increase. The map P: $C \rightarrow P$ then allows the thermal transformation of A to be represented by the path $P(A(t))$ on P. Conventionally the parameter t is the time since initiation of the reaction, or alternatively the reaction path can be parameterised by α, the fractional progress of the transformation. The requirement that such paths exist will not impose more than simple constraints on the structure of P, if we allow the possibility that such paths might not be smooth or continuous (as might be the case, for instance, at a phase transition). The tangent vector $\mathrm{d}P(A(t))$, where it exists, to a path passing through $P(A(t))$ is then an experimentally-determined rate equation for the chemical system with properties $P(A(t))$. This is so because the n-dimensional tangent vector to the path $P(A(t))$ has as its components the rate of change with the parameter t of the n different properties of the sample. Given a suitably-defined space P of properties and theoretically-derived rate equation $\mathrm{d}R$ at each point in P, showing how these properties change locally, one has enough to predict how the properties of a set of substances evolve through time. Typical practice is to relate a measured property, such as the sample mass m, to the extent of reaction, α, via some relation $m(\alpha)$. The rate of transformation, $\mathrm{d}\alpha/\mathrm{d}t$ is related to a conversion function, $f(\alpha)$, by $\mathrm{d}\alpha/\mathrm{d}t=k\,f(\alpha)$ where the rate coefficient, k, depends on T, E and the pre-exponential factor, A. Hence, the rate equation for m, $\mathrm{d}m/\mathrm{d}t=(\mathrm{d}m(\alpha)/\mathrm{d}\alpha)$, $\mathrm{d}\alpha/\mathrm{d}t=k(\mathrm{d}m/\mathrm{d}\alpha)$, $f(\alpha)=k\,f'(\alpha)$.

The notation $(P, \mathrm{d}R)$ groups P, the space of properties, and $\mathrm{d}R$, the set of rate equations applying to P, together as a single object, in this case the theory of thermal transformations of the systems in C.

Now, the theory gives us a way of modelling the thermal transformation of any system A in C. $P(A(0))$ is the set of properties of A at time zero. $R(p, t)$ is the path, originating at a point p in P, which is obtained by integrating the rate equations $\mathrm{d}R$ along the path. The form of the path can be related to the conversion function, $g(\alpha)$. For the theory and the experimental measurements to agree perfectly, the experimental path $P(A(t))$ and the theoretical path starting at the same point $P(A(0))$, that is $R(A(0), t)$, should be the same.

If we accept the inevitability of some error in prediction, then $(P, \mathrm{d}R)$ may still yield a 'useful' theory of the thermal stability of the systems in C. How can we determine whether $(P, \mathrm{d}R)$ forms a useful theory of thermal stability for the systems in C? Although final confirmation of the (non-)utility of any theory relies on experimental verification, some of the characteristics which may preclude certain formalisms from ever, even in principle, yielding a useful theory of the thermal stability of solids can be explored. To measure the utility of any theory $(P, \mathrm{d}R)$ we need a measure of the closeness of points in P. (For example, on the plane, one possible measure is the straight-line distance between points, another is the, possibly weighted, sum of absolute values of co-ordinate changes between points.) If A and B are two systems represented as points a and b in P (Fig. 2a), then let $|a, b|$ measure the 'distance' or 'difference' between A and B (according to theory $(P, \mathrm{d}R)$). Define a theory as 'reliable on set C', if it yields reaction paths which are sufficiently close to the measured reaction paths for all systems in C. In other

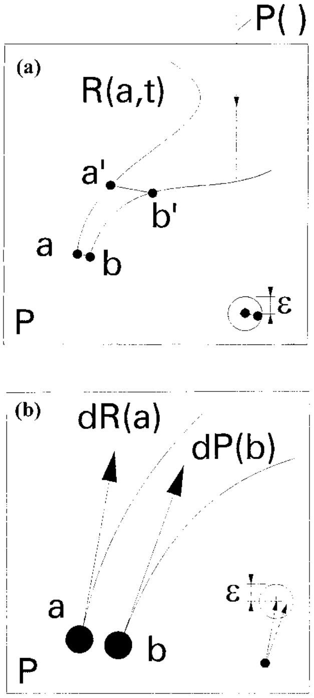

Fig. 2. Schematic showing the definition of the reliability of a theory in terms of the distance between theoretical and experimental reaction paths: (a) global; (b) local.

words, for suitably small distances, δ and $\in$, $|P(A), b|<\delta$ should imply that $|P(A(t)), R(b, t)|<\in$ for all time and for all systems A in C. Now, any theory which yields paths which are not stable to small changes in starting point (the internal equivalent to small errors in measurement) cannot be reliable on any set of chemical systems under the given definition. In other words, if a and b are in P and $|a, b|<\delta$ yields finite $|R(a, t), R(b, t)|$ after a certain amount of time, no matter how small δ becomes, then the predictive ability of the theory will fail. This mode of failure of a given theory is associated with the oft-cited possibility of chaotic evolution which can occur in the presence of nonlinearity in the rate equations if P has dimension greater than two (with obvious implications for systems where the reaction mechanisms have multiple intermediate steps).

Note, though, that this definition of reliability is difficult to apply in practice, since it relies on the determination of non-local characteristics of the theory (P, dR). When trying to apply a non-local restriction, one has to examine each experimental and theoretical path passing through each of the points in P of interest. A non-local measure of reliability, thus, requires the rate equations to be integrated and can be much more trouble to calculate than a measure of reliability based on extracting information which is already given in the package (P, dR).

The best we can generally hope for is to apply a local definition (local in the sense of being defined using information specified at single points of P, that is, using the rate equations and not the paths generated by the rate equations) of the reliability of any given theory. In Fig. 2b, let (P, dR) be 'locally reliable on set C', if $|P(A), b|<\delta$ implies $|\mathrm{d}P(A)-\mathrm{d}R(b)|<\in$ for suitably small and $\in$ and for all systems A in C. So, instead of requiring that the theoretical and experimental paths do not diverge by more than a certain amount after a certain time, we require only that at any given point of P, the tangent vectors to those paths do not point in different directions by more than a certain amount. Note that the local definition is less restrictive than the global one, and, for instance, will classify many theories which are subject to chaotic evolution as reliable.

A more interesting way in which the reliability of a theory (P, dR) can be compromised results if the theory omits a property with significant effect on the thermal behaviour of the systems in C. In this case, the theory (P, dR) may possess reasonable properties in its own right but might fail to provide reliable predictions of the thermal behaviour of the systems in C. The question is then whether the theory can still be shown to be reliable on some subset of C, or conversely whether a theory constructed from some subset of C can be shown to be reliable on the whole of C. Assume the existence of two theories (P', dR') and (P, dR) both purporting to describe the thermal behaviour of the systems in C. Now assume that P is of smaller dimension than P' through the omission of some set of the properties of the systems in C, but that the effects of the unresolved properties are retained in P through the map M from P' to P being a projection (Fig. 3). For example, the space P' might be a space representing the three properties temperature–pressure–concentration, and P might be a space representing only temperature–pressure. The projection from P' to P is simply the rule we use to take each point representing temperature–pressure–concentration and to convert it into a point representing temperature–pressure.

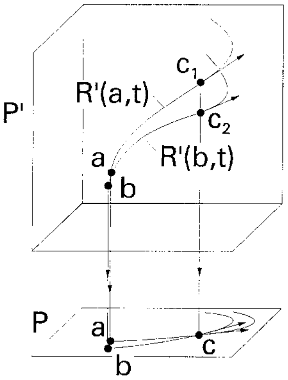

Fig. 3. Schematic showing how inappropriate projection can lead to non-uniqueness of the rate equations.

Let the projection M map at most m points of P' onto any point in P (Fig. 3, only two of the curves which project points onto the lower dimensional space are shown). Then any reaction path R' in P' projects onto a reaction path R in P, but at any point p in P, the projection yields at most $m'\times m$ distinct reaction paths (accounting for the possibility that the theory (P', dR') might inherit m' distinct reaction paths at each point p' of P' by projection from a theory incorporating an even more comprehensive set of the properties of the systems in C) and hence $m' \times m$ distinct sets of rate equations at each point in P.

If the theory (P', dR') is used as a model for the experimental system (setting $m'=1$), then M models the idealisation by measurement, P: $C \rightarrow P$, and a measure of the usefulness of the theory (P, dR) in the presence of unresolved properties of the systems in C can be estimated. Two properties of (P, dR) characterise the reliability of the theory. Firstly, a measure of the scatter of the curves $P(A(t))$ passing through any point p in P. This property gives an estimate of the utility of P as a condensation of the dynamic behaviour of the systems in C, in the sense that minimal scatter suggests that the space P is large enough to capture adequately the physical properties which are relevant to the observed dynamic behaviour of the systems in C. Secondly, a measure of the distribution of curves $P(A(t))$, passing through any point p in P, around the theoretical curve $R(p, t)$ provides an experimental measure of the local reliability of theory (P, dR), that is, the ability of the theory (with a single rate equation defined at each point of the property space) to capture the behaviour of all the systems which have the particular properties defined by that point.

Practically, the first of these two measures can be defined as:

$$\sigma^2(p) = \sum_C \int_t \delta(A(t) - p)|\mathrm{d}P(A(t)) - \mu(p)|\mathrm{d}t$$

where

$$\mu(p) = \sum_C \int_t \delta(A(t) - p)\, \mathrm{d}P(A(t))\mathrm{d}t$$

and the second measure can be defined as:

$$\chi^2(p) = \frac{\sum_C \int_t \delta(A(t) - p)|\mathrm{d}P(A(t)) - \mathrm{d}R(P(A(t)))|\mathrm{d}t}{\sigma^2(p)}$$

Where $\delta(p)$ is the Dirac delta function suitably constructed on P.

Fig. 4 is a schematic illustration of the geometric interpretation of the unreliability, χ^2, and scatter, σ^2, of a theory (P, dR). σ^2 is a measure of the scatter of the experimental vectors, whereas χ^2 is a measure of the deviation of the bunch of experimental vectors from the theoretical vector for that point. The first measure becomes the variance of the experimentally-measured values of the rate equations if the space P is one-dimensional, we divide by $N-1$ (where N is the number of members of C) and the distance measure $|a, b|$ is given by $(a-b)^2$. Similarly, the second measure reduces to a Chi-squared test: the predicted rate equation is being tested for its lack of conformity with a set of experimental data. Hence, χ^2 may be termed the unreliability of the given theory. Conversely, when a conversion function that best fits the data is chosen, a distance measure is being applied to the property surface to select a theory which minimises the unreliability χ^2. The one-dimensional example just described, with the distance measure selected such that $|a, b|=(a-b)^2$, is of course equivalent to least-squares fitting of a theory to the available data.

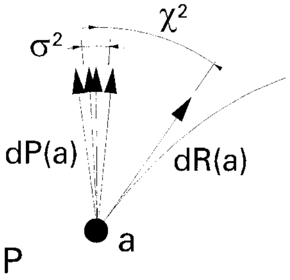

Fig. 4. Schematic illustrating the geometric interpretation of the unreliability, χ^2 and scatter, σ^2, of a theory (P, dR).

3.1. Predicting the behaviour of an untested material on the basis of the information available for similar materials

Extrapolation onto untried regions of the property space requires assumptions as to the smoothness of the reliability measures near the point of interest. In other words, if the unreliability is low for 'similar' materials (subject of course to the problem of defining similar) then one might expect the unreliability not to change much if we move to an untested, but similar material (i.e., one nearby on the space of properties). For example, the properties of barium carbonate may lie in a region of property space where the 'theory of barium salts and metal carbonates' has low 'unreliability' and low 'scatter'. The problem is that one does not know whether the unreliability changes quickly or slowly as one moves onto uncharted territory. There may be some fundamental unexpected, but hidden property of the new material which would force the introduction of say, a completely new dimension into the property space (i.e., a new variable into the theory) which might then force the definition of distance measure in the higher-dimensional theory to acknowledge the fact that the new substance was not as close to the original set of substances as was at first believed. The analysis can, thus, show on what parts of the set of systems C, the theory works well, but it requires assumptions of slow-varying scatter and unreliability to extrapolate from measured data into the unknown, and hence to expand C. This is the key to whether an adequate theory can exist. What confidence can we have that extrapolation will not get us into trouble, even given that the theory behaves well on certain parts of P?

In Fig. 5, the thick black curves represent the typical experimental situation where one has measured the reliability of the theory only along the reaction paths for which one has been able to do the experiment. So in general, one has patchy coverage of the reliability of the theory (generally along curves through P) from which it is exceedingly difficult to construct a global picture of the reliability parameters or of their rates of change away from the measured data. (This is principally because one can really only measure the gradients of the parameters along the curves, and cannot measure the gradients transverse to the curves.)

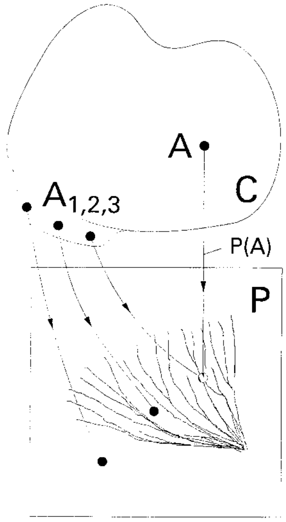

Fig. 5. Schematic showing extension of the theory to a new substance.

So, if one tries to apply the theory to three candidate points, Al, A2 and A3 in Fig. 5, Al and A2 fall directly into unmeasured areas with completely unknown reliability, but even A3, which falls very close to a known area (or even into a known area) will cause problems because of the possible effect of omitted properties discussed above.

4. Conclusions

A lot of attention in decomposition studies has been directed towards somewhat mechanical kinetic analysis, rather than in establishing the factors that control reaction rates, such as the influences of heat and mass transfer within the reactant mass, reaction reversibility, inhomogeneities within the reactant mass, etc.

Many studies (isothermal or non-isothermal) have been regarded as complete when the statistically most applicable rate equation has been identified and the apparent Arrhenius parameters have been calculated. Microscopic examinations, capable of confirming geometric conclusions, and the use of other complementary techniques are not always attempted.

Techniques have been suggested for probing the chemical processes in the reaction interface more directly, but most, in principle, are likely to introduce further uncertainties by interfering in the normal processes, for example, wet chemical analysis of reaction intermediates in a crystolysis reaction involves assumptions that solvents and reagents used can reach the reaction interface and remove the species of interest without producing other effects. Even less molecularly invasive spectroscopic techniques depend on producing and measuring some response in the active species and the excitation, as in homogeneous reactions, will generally change the normal course of reaction. Vyazovkin and Linert [12] have indicated ways in which spectral data may be applied to support kinetic observations in identifying the rate limiting step. This particular work was not concerned with a crystal decomposition but future development may extend work in this direction. Examination of the evolved gaseous products of decomposition, using a sensitive analytical technique, such as mass spectroscopy or Fourier transform infrared spectroscopy, has been rather neglected [13].

The discussion above illustrates the need to measure the changes in as many as possible of the properties of a reactant during the course of decomposition. For example, comparison of the rate of heat absorption or evolution with the rate of mass loss during decomposition can immediately warn of a change in reaction mechanism. Continuous monitoring of crystal structure can reveal other asynchronous processes. The influence of unresolved factors would be that the kinetic results for repeated experiments, on ostensibly the same material, would vary in some unpredictable way. The more sensitive the system is to the unresolved factors, the greater the variability in the outcome of a series of experiments. One could then quantify the sensitivity to unresolved factors by some measure of the scatter in the results for a series of experiments.

Science progresses by reiterative examination of simplified models of real processes as the number and type of simplifications are decreased. The decompositions of alkaline-earth carbonates [14] and peroxides [15] have been modelled recently by de La Croix et al. by devising symmetry-controlled routes for transforming the reactant structures into those of the solid oxide products. Lattice energies of the reactants, of the conjectured transient intermediate structures, and of the final products were estimated and profiles of energy changes during the proposed decomposition routes were constructed. Barriers in these energy profiles are compared with experimental values reported for the activation energy of the thermal decomposition. This is a relatively crude model but is computationally accessible. Several paths for the processes were examined and the energetic consequences thereof were calculated. Those mechanisms which yield an activation energy which is greater than the experimental value are feasible, even if not necessarily realistic. Those mechanisms with an activation energy lower than the experimental value are kinetically inaccessible and must be rejected. This is not unlike the procedure in the development of mechanisms of homogeneous reactions, where the proposed mechanism must fit the experimental kinetic observations, but is not thereby proven.

L'vov's interesting recent work [16–24] is based on the proposal that decomposition involves an initial sublimation step. For ionic compounds this corresponds to the process on which the calculation of lattice energies is based:

$$\mathrm{AB(s)} \rightarrow \mathrm{A}^{n+}\mathrm{(g)} + \mathrm{B}^{n-}\mathrm{(g)}$$

followed by condensation of the less volatile products. Because sublimation is an endothermic process, the condensation process would have to play a major part for a decomposition to be exothermic overall.

The models used for the decompositions of solids (crystolysis) have brought the subject quite a long way, but the complexities of the real processes appear to be too great for the models so far considered?

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