

## KINETICS OF THERMAL DECOMPOSITION OF THE SOLID STATE. II. DELIMITING THE HOMOGENEOUS-REACTION MODEL

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### ABSTRACT

Present evidence shows that many thermal processes can be described by the generalized rate equation

$$-dx/dt = Z \exp(E^*/RT) f(x)$$

but many others cannot. Still others may be adequately describable by a modified equation. A small set of tests will enable the experimenter to determine whether or not the equation applies. These include change of sample size, change of sample geometry, and extended time of reaction.

### A. STATEMENT OF THE PROBLEM

#### *Mathematical inconsistencies*

In a previous paper [1], the question of existence of just two kinds of kinetic behavior, viz., those describable by homogeneous kinetics, including the Arrhenius equation, as compared with those which are not at all describable by these concepts, was examined. With so many arguments in the thermal analysis community about kinetics in general and about specific processes, it should be obvious that many, and possibly most, participants have some firm basis for their confidence in their own practices. There is one circumstance to face—even though an investigator is absolutely certain that the assumptions he or she uses are completely valid for *his or her* system, quite different calculations and assumptions adopted by other people may be just as correct for the systems *they* study. That is, there may be more than one class of materials, some being describable by fairly simple treatments of the data, but some not. It does not follow, however, that there is a simple dichotomy: processes describable by homogeneous kinetics vs. processes describable by some other single type of kinetic approach, such as diffusion-limited topochemical reaction. This might be true, but delineation will not be resolved by continued dispute; the question ought to be resolvable.

ble by more meticulous testing and reporting of kinetic data. The present evidence shows that the true condition is not that simple; there are certainly the two categories, but they certainly do not include the whole range of thermal decomposition processes.

There are some weaknesses inherent in the present treatments used to justify particular mechanisms. The goal of this present paper is to show that these deficiencies can be revealed very easily by a small number of simple tests. Then, from critically tested data, a firmer understanding of solid-state decomposition kinetics should emerge.

Separation of treatments of processes is imperative to determine which processes can survive the tests, and both (1) continue to be describable by homogeneous kinetics, and (2) yield reproducible kinetic parameters from laboratory to laboratory, as well as from instrument to instrument. Determination of the true status of each process will then lead to more accurate description of that process and improved understanding of kinetics in general.

To emphasize the need for experimental determination of the true status of a process, it is worthwhile to draw attention to some of the deficiencies in popular treatments that were not covered thoroughly in the earlier work [1].

Application of homogeneous-kinetics computations to solids was initiated in the 1940's and extended in the next two decades, with a number of minor variations offered in later years [2–17]. Some publications have criticized or expressed doubts about the application of homogeneous kinetic concepts to heterogeneous processes [18–25], but these are still a small minority. There are some firmly based theoretical objections to use of the homogeneous-kinetics rate equation for a large number of specific reactions; on the other hand, there is firm support from data on some other reactions. It is because there is no simple yes-or-no general answer that we must evaluate each system.

The use of a rate of reaction that is proportional to some function of the reactant concentration, i.e.

$$\text{rate} = k'f(C) = kf(x) \quad (1)$$

in which the effective concentration can be expressed as the unreacted fraction  $x$  of the initial material and the rate 'constant'  $k$  is a statistical function of the temperature  $T$ , described by the Arrhenius equation

$$k = Z \exp(-E^*/RT) \quad (2)$$

is clearly inappropriate if there is evidence of any phase boundary. The material reacting has no knowledge of the amount of unreacted material remaining behind the reaction front. But further, and vitally important, eqn. (1) states explicitly that there is no variable other than  $x$  that affects the rate of reaction.

Equation (2) implies a symmetric distribution of energy states above and below some mean (and most probable) value, but this is not in accord with

our knowledge of the solid state, the perfect crystal having the lowest energy at a given temperature. One might argue that some Boltzmann-like distribution does exist, but this would require that the mean energy *and* the most probable state exist at vibrational energy states several steps up from the ground state. This would be a remarkable phenomenon.

Also, the quantity  $Z$  has come to be known as the ‘pre-exponential factor’, rather than the ‘frequency factor’. In homogeneous kinetics it relates the fraction having the requisite energy to react to the observed rate of reaction. No matter what we call it, it still performs this function. From consideration of its meaning, there is no reason to expect any substantial change in value due to changes in experimental conditions. Certainly it should not change with sample size, yet we see such reports [26]. Or with heating rate, yet we see such reports [27]. There is even a report of a ten-million-fold change as a result of a change in atmosphere—even though neither gas was a reactant or product [28]. Any unreasonable variation of the factor  $Z$  should alert the experimenter that the assumptions he or she has used are incomplete, or possible even incorrect.

Equations (1) and (2) are generally combined into a single equation and used to compute kinetic parameters for many kinds of processes, without any attempt to verify the form of the kinetic equation. This ‘generalized’ rate equation is then the starting point of a determination of the reaction model, ordinarily without any critical examination. The equation can be expressed in the form.

$$-dx/dt = Z \exp(E^*/RT)f(x) \quad (3)$$

which is simply a substitution of terms, and still has all the strengths and weaknesses of the initial statements. This generalized equation is used to defer the selection of a kinetic equation until some relatively easy comparisons with experimental data can be made, using the assumption that the equation yielding the closest fit provides a definitive description of the process—again without any critical test.

The major difficulty with this procedure is that quite a number of the proposed equations yield curves that are so nearly alike that the final selection becomes very largely subjective. Some variations have been derived that appear to give better delineation of rate equation forms, but they are based on the same assumptions and have the same strengths and weaknesses. A clear delineation might be obtainable using the derivative of the rate, as proposed by Selvaratnam and Garn [29]. In this plot, agreement with a model provides a much more critical test than is customary because the theoretical curves show clearer differences. If the generalized equation procedure is chosen, however, the validity of the selected rate equation can be tested by the experiments described below.

Being derived from eqn. (1), the generalized equation recognizes only one variable,  $x$ , the fraction remaining. It should be obvious that if the measured

values are dependent upon the sample size or its containment, some characteristic of the apparatus is actually being measured. Generally this will be heat transport. Indeed, the smaller the sample, the greater the dependence of the measured data upon the instrument parameters.

### *Reaction front*

For many materials, particularly inorganic crystalline species, examination of a partly reacted material will disclose a zone of reacted material on the outside of the particle, or sometimes on the outside of a multiparticle specimen. It is completely clear that the reaction is not taking place uniformly throughout the sample, and hence the assumption of homogeneous kinetics fails for these materials. The concept is not new [30] nor has it been discarded. Prodan [31] has recently discussed topochemical processes in some detail.

In these cases, the reaction may be limited in rate by diffusion of gases away from the reacting interfaces, but it may also be limited by diffusion of heat to the interfaces or a combination of both effects. Diffusion of gases is often irregular because dimensional changes may lead to physical cracking, which is probably not uniform or smoothly changing with time. Magnesium hydroxide, for example, starts to decompose by formation of water molecules within a hydroxyl layer [32–34], followed by dehydration of that layer, then enough others to induce cracking, then dehydration of the newly exposed surface, etc. [35]. Even so, there are reports of order-of-reaction and other models for magnesium hydroxide [36–41].

Limiting the diffusion models to collections with uniform geometry and size is not productive; it divorces the computation from reality. Simple or uniform geometries are seldom encountered in practice, and should not be accepted even as approximations without experimental evidence.

### *Reversible / irreversible processes*

It is already well established that for many inorganic decompositions the atmosphere (or specifically the pressure of the gaseous product) establishes the temperature range of the decomposition. It is also well established that this is not true in all cases; some materials decompose over a small temperature range under any ordinary experimental conditions. Dolomite, for example, undergoes its first decomposition at quite consistent temperatures near 700 °C in vacuum, air or carbon dioxide [42], whereas the decomposition of anhydrous calcium oxalate proceeds ca. 450 °C under a similar range of conditions. There are substantially varying reports about kinetic models for calcium oxalate, all using established models and none including critical testing [43].

For all reversible decompositions, and even for some irreversible decompositions, a change in the atmosphere or in its pressure will cause a change in the rate of reaction at a given temperature, although the form of the curve may remain the same [44]. Changes in the degree of confinement of product gases can have similar effects [45]. There is no question that the generalised rate equation, as expressed in eqn. (3), fails for these materials.

In the organic/polymer field, there are at least some reversible reactions. One well-known example is poly(vinyl chloride), for which confinement of the vapors or supply of hydrogen chloride will have a marked effect upon the progress of the reaction.

Many of the decomposition steps, though, are not reversible. Some also require little energy input so that temperature gradients are not great. For these and some of the inorganic processes, adequate testing will probably establish the generalized rate equation as descriptive, or provide information that can lead to successful modification of eqn. (3).

### *Atmosphere effects*

For all reversible decompositions, and even for some irreversible decompositions, a change in the atmosphere or in its pressure will cause a change in the rate of reaction at a given temperature, although the form of the curve may remain the same [46]. Changes in degree of confinement of product gases can have similar effects. There is no question that the generalized rate equation fails for these materials, but it may be possible to incorporate a suitable pressure term. Mere application of high vacuum does not remove the pressure from consideration. Wiedemann illustrated this in his curves for calcium oxalate monohydrate [47], wherein the two reversible processes showed a clear downward temperature progression as the chamber pressure  $p_c$  was decreased from atmospheric down to ca.  $10^{-4}$  mmHg. The decomposition temperatures at lower pressures were almost constant because the diffusion of water vapor, then of carbon dioxide, within the specimens became the limiting process, the pressure  $p_r$  at the reaction interface remaining almost constant. This occurs whenever  $p_c$  is smaller than  $p_r$ . The actual rate of reaction is limited by the transfer of heat.

## B. EXPERIMENTAL EFFECTS

### *Particle size*

For many materials, the experimental data show that the rate of decomposition of particulate specimens of different sizes from the same sample source varies significantly. The particle size is not one of the variables in the rate equation, so eqn. (3) fails, or is incomplete, for these materials. Simi-

larly, a change in surface area will effect a change in the rate of reaction for many materials. If it does, the rate equation fails or is incomplete.

### *Homogeneity of energy*

For many materials, particularly inorganic, the thermal energy uptake by a specimen changes drastically as a typical endothermic process takes place. Transfer of heat requires a temperature gradient, so a rapid process, particularly one that requires much heat, cannot be assumed to be at a uniform temperature throughout. There is generally a reaction boundary whose movement through the sample is principally dependent upon the heat transfer characteristics of the furnace assembly, so eqn. (3) fails. On the other hand, a low-energy or a slow process might very well have a negligible gradient, so that an assumption of uniform temperature may be quite adequate for such processes.

## C. SYSTEMS DESCRIBABLE BY HOMOGENEOUS KINETICS EQUATIONS

### *Need for examination of processes*

An understanding of the deficiencies in the universal application of homogeneous kinetics does not require the abandonment of the Arrhenius equation, as Adonyi and Korosi [48] inferred from our criticism [49] of the kinetic compensation effect (KCE). The KCE is simply a consequence of trying to describe a complex process by computing one of the two constants in eqn. (3) and dumping the results of computed variations into the remaining 'constant', accepting changes of many orders of magnitude without question or test [50–52]. The tests (described in Section D) that ought to be routine would verify the KCE if it is real.

The validity of the Arrhenius equation in processes known to be homogeneous is well established. The quest here is to ascertain to what degree its use can be extended to systems that are not truly homogeneous.

### *Probably-homogeneous reactions*

Viewing the reacting material from another perspective can be helpful. Non-crystalline materials in condensed states can be considered as solutions whose components fall into two groups, solutes and solvents, a solvent being the principal constituent whether or not there is another component. The solution may have any degree of fluidity. Consider now a solution in which the solute will decompose at a lower temperature than the solvent. From this perspective, the solvent can be seen as the medium for heat transfer and temperature change, whereas the solute molecules or ions or other species

simply respond to their environments by reacting at the appropriate time or circumstance. Further, the non-crystalline solvent has a higher total energy than the corresponding crystalline solid; that energy, however, is not uniform. There is no reason to expect the various energies to have a systematic distribution, but it is reasonable to expect only a small range of energies. If the solute is quite dilute and randomly distributed, we may assume that its individual units will also have energies distributed about some mean value, randomly above and below that mean value, and with small deviations more probable than large deviations; in short, a probability curve of the same form as is used in describing homogeneous kinetics. From this perspective, in liquid or solid solution there is a rational explanation for the agreement of experiment with homogeneous kinetic calculations and a basis for calculating the kinetic parameters.

### *Reaction of principal component*

Turning now to the principal component (matrix), ranges of behavior have been observed, and these differences have divided workers largely into two groups, each completely confident that homogeneous kinetics *is not* or *is* descriptive of real systems and imperceptive of any validity of the other view. The confidence of each group has been generally soundly based in that there are many systems (most inorganic decompositions) for which eqn. (3) is without merit and many others (polymeric and other glassy systems) for which it appears to be well founded.

As discussed above, the matrix (the principal material with or without a solute) is *ab initio* a part of the heat transfer system, providing or accepting the heat involved in the solute reaction. When the matrix itself is using or giving up the heat of its own decomposition, its physical changes will grossly modify its behavior. Assuming an endothermic process that could occur homogeneously, the heat is being transferred through a surface and surface layers whose properties are continually changing. (For boundary processes the change is to a discrete new state, but the thickness is changing.) Yet there are reactions that appear to be clearly describable by homogeneous kinetics.

These homogeneous-kinetics processes may be limited to relatively low and endothermic enthalpy changes plus exothermic reactions. In polymers, for example, there are specific types of reactions that can be expected to occur more or less randomly. Scission at some point of strain (high energy) is more probable than in an unstrained segment. Cross-linking will occur most readily at points where the functional groups involved happen to be well positioned, with continued reaction as chain movement brings others to the appropriate contiguity; this should be true both for direct chemical interaction and for free-radical processes. In short, there are common

reactions of the matrix whose characteristics could render them clearly describable by homogeneous kinetics.

#### *Possible extension of generalized rate equation*

Another possibility exists: namely, some of the processes could be described by the generalized rate equation if the function statement was complete. That is, for processes whose decomposition temperature depends strongly upon the pressure of the product gas, an  $f(x, p)$  may be available that would include the pressure in the proper mathematical form. Similarly, for some processes, a term in surface area per gram or per mole might enable an otherwise deficient equation to describe the process precisely. Without critical testing, however, there is no way to know whether or not some modification is needed or would be useful.

#### D. DELINEATION OF PROCESSES

##### *Variations during data gathering*

Tests to determine the continuity of any process are virtually absent from the literature, yet the possible tests are simple. Some have been proposed before [20,21]. Especially when the kinetic model to be ascribed to a process is being chosen simply for closest conformity to a calculated curve, a test should be used to assure the experimenter that the model does indeed describe the process satisfactorily. Besides examination for homogeneity during reaction, two very simple tests are (a) change in sample size by the largest factor that is reasonably convenient, and (b) change of the sample geometry or enclosure. Each of these can be performed without even a change of programming. They guard particularly against overlooking heat and mass transfer as the reaction rate limits. Finally, tests of computed parameters should verify the reaction model inferred, and that reaction model should be rational for that process. The tests are detailed below.

##### *Examination for homogeneity*

Whenever possible, a fractionally reacted (e.g.  $x = 0.6-0.7$ ) specimen should be examined to ascertain whether or not there is evidence for a second phase on its exterior. For some materials, microscopic or even spectral inspection may be helpful. The result should aid in determining whether or not a diffusion, nucleation or growth reaction-rate limit must be considered.



### *Change of sample size*

A change of sample size by a factor of four ought to be possible in any apparatus. Close correspondence of rates should be expected. Significant variation will suggest that some other variable must be considered.

### *Change of sample containment*

Use of an open versus a closed sample holder should lead to variation in rate if there is some atmosphere effect that should be taken into account. Simple spreading into a thin layer as compared to a more compact specimen will affect the rate only if there is either an atmosphere or a heat transfer term missing.

### *Extended-heating tests*

After initial data gathering has enabled selection of an appropriate kinetic equation and computation of the kinetic parameters, the values should be tested by calculating a temperature at which the reaction will proceed substantially, but not nearly completely, in several hours—overnight, for example. Agreement of actual reaction degree with that calculated would provide good evidence that the computed parameters are meaningful.

### *Rationality of the selected model*

There are some incompatibilities that must be recognized; for example, a first-order reaction is not compatible with formation of a different product on the exterior. Likewise, clear evidence of homogeneity would lead to serious questioning of a diffusion limited model.

## E. CONCLUSIONS

These tests ought to be done before even reporting values within one's own organization, for example for processing planning. For those cases in which the generalized rate equation holds, the form of the curve and the temperatures at corresponding degrees of completion will be the same and the calculated kinetic parameters will agree very well.

Certainly the tests should be used to verify a kinetic model before it is represented as a truth to the scientific or engineering communities. There are already enough discrepant reports about which we can engage in disputes. New information should not simply present a different model or just supply another vote for some already proposed model; the new information should include firm evidence that the chosen model is the correct and only model.

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