Thermochimica Acta, 135 (1988) 71–77
Elsevier Science Publishers B.V., Amsterdam

KINETICS OF DECOMPOSITION OF THE SOLID STATE: IS THERE REALLY A DICHOTOMY?

PAUL D. GARN

The University of Akron
Akron, Ohio, 44325, United States of America

ABSTRACT

Within the thermal analysis community, the predominant concept of kinetics of decomposition of solids is an adaptation of homogeneous kinetics as derived and confirmed for (in particular) reactions in the gas phase and extended to the liquid/solution phase. There are some obvious objections to use the concept for a large number of specific reactions, but there is also enough support for many other reactions that its untruth is no more proven than its truth.

When a sample is reacting at a surface, its rate cannot be dependent upon the amount of material behind that surface; the concept of the rate as function of the amount unreacted cannot be justified. Introduction of special particle geometries by which an actual zero-order reaction appears to fit some order-of-reaction equation is a mathematical convenience that is misleading.

The Arrhenius equation is not descriptive of the energy distribution in solids because the "molecules" cannot maintain a statistical energy distribution nor is the required symmetry possible, so the calculated variations of rates as functions of temperature are generally inaccurate.

Tests of particular processes by simple and fairly-convenient changes in procedure will disclose whether or not the specific process is describable by the conventional kinetics. Even so, some processes appear to survive the tests and some appear neither to fit well nor to fail badly. These may all be multistep reactions that cannot be resolved sufficiently well to calculate realistic kinetic parameters. The way to establish the boundaries of our standard treatments is to test their validity for each process as a matter of course, as compared to defending their derivations against criticisms.

Invited Lecture.
Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

GOAL

The intent here is to present an explanation of the need for more-nearly-complete reporting of kinetics experimentation and data interpretations. Some uncertainties inherent in present treatments can be vitiated by a small number of simple tests to unearth deficiencies in the model. From critically-tested data a firmer understanding of solid-state decomposition kinetics may emerge.

PRESENT ORTHODOXY

Homogeneous Kinetics. Within the thermal analysis community, the predominant concept of kinetics of decomposition of solids is an adaptation of homogeneous kinetics as derived and confirmed for reactions in the gas phase and extended to the liquid/solution phase. Its application to solids, with an array of simplifying assumptions, was initiated in the 1950s and extended in the 1960s, with a number of minor variations offered in later years. There are some obvious objections to use of the concept for a large number of specific reactions, but there is also enough support for many other reactions that its untruth is no more proved than its truth. The principal goal of this presentation is to examine whether or not

a. a single type of kinetic description is applicable;
b. a second type is needed for some cases; or
c. still more descriptions may be needed.

The concept of homogeneous kinetics is based upon a rate of reaction that is proportional to some function of the reactant concentration, i.e.,

$$\text{Rate} = k\ f(C), \tag{1}$$

in which the effective concentration can be expressed as the fraction x of the initial material and the rate "constant" k is a statistical function of the temperature T, described by the Arrhenius equation,

$$k = Z \exp\,[-E^*/RT]. \tag{2}$$

Generalized Rate Equation. Using a number of assumptions, the considerations listed above have been combined into a single equation and used to compute kinetic parameters for many kinds of processes. This generalized rate equation is often the starting point of a discussion without any critical examination whatsoever. The form can be expressed as

$$-dx/dt = Z \exp\,[E^*/RT]\ f(x), \tag{3}$$

which is simply a substitution of terms and therefore has all the strengths and weaknesses of the initial statements. A clear understanding of the assumptions is critical to the assessment and effective use of the generalized rate equation and to determination of whether or not it is the correct equation for a particular case. Equation (1) states that the rate of reaction

is a function *only* of x; that is, no other effect exists that will lead to a significant change in rate. Equation (2) describes a system in which there is a symmetric distribution in energy about — i.e., above and below — the mean energy, this mean energy being also the most probable state.
The term E^* describes the breadth of the distribution curve; in homogeneous kinetics this provides a measure of the fraction of the entire number that have the extra energy (above the mean energy) to exist in an "activated state". Equation (3) avoids an *a priori* statement of the reaction form; that form is "determined" by substitution of standard forms until some form is chosen as providing the "best fit" to the experimental data.

Several model reaction forms are generally tested, the principal types being order-of-reaction and nucleation-and-growth. The order-of-reaction models assume homogeneous kinetics, i.e., the reaction proceeds uniformly throughout the sample. The rate is an exponential function of x and the exponent may be fractional as well as integral. Nucleation-and-growth models assume that there are processes that begin at random points on the surface of each particle and grow uniformly in two or three dimensions, at rates still describable by the probability curve and an $f(x)$. The nucleation may be assumed to be a continuing process, new nuclei being formed at a rate that is a function of temperature. The growth may be assumed to be constant but it has been mathematically related to x for specific geometries. Alternatively, single nucleation may be assumed for each particle with the growth of the reacted zone being the limiting step.

WEAKNESSES OF KINETIC TREATMENTS

Observed Rate Proportional to f(x)? The mathematical term $f(x)$ states explicitly that there is no other variable; if $k = f(x)$ is to be true, there can be no change in rate by reason of any variation in instrumental parameters, in atmosphere, in shape, in size or anything else. When changes in rate are observed from any cause other than variation in temperature (i.e., in k) or progressive depletion of the reactant, this rate equation fails. Some other form, $f(\ ,\ ,x,\ ,\ldots)$, which included all parameters having significant influence, would be needed.

Accuracy of Measured Temperature. In all cases using samples that are small enough that the temperature must be measured outside the specimen itself, the added demand for heat when a decomposition has begun will change the temperature distribution so that the actual temperature of any point in the sample has a different relationship to the measured temperature than during simple heating. For samples large enough that the interior temperature can be measured, that demand leads to a slowing of the temperature rise and a measureable gradient within the sample; for small samples, a gradient exists but is ignored. In either case, some correction can be applied, but it must be recognized that the measured temperature does not represent a uniform temperature throughout the sample, the error varying in direct relation to the heat of reaction. Uniform temperature may, however, occur in exothermal reactions that proceed slowly.

Statistical Distribution of Energies. Within some kinds of materials it is reasonable to infer a distribution of energies, some higher and some lower than the most probable state. It is even possible to hypothesize a smooth and symmetric distribution describable by a probability curve such as the Arrhenius equation. For others, however, a symmetric distribution is quite impossible. Thermodynamically, a completely ordered crystal is already at the lowest possible energy for that material at that temperature. A basic assumption is invalid, so the Arrhenius equation fails for these materials.

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 an incompletely-reacted particle or sometimes on the outside of a multiparticulate specimen. It is completely clear that the reaction is not taking place uniformly throughout the sample and hence the assumption of homogeneous kinetics fails. It will often be apparent that the nucleation-and-growth models also fail.

Particle Size/Surface Area. For many materials, the experimental data show that the rate of decomposition of particulate specimens of different sizes from the same sample varies significantly. The particle size is not one of the variables in the rate equation, so it fails for these materials. Corollary to the particle size variations, a change in surface area will effect a change in the rate of reaction for many materials. Again, the generalized rate equation fails.

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. 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.

Changing Rate-Limiting or Concurrent Processes. In addition to the intrinsic uncertainties in the generalized rate equation for a single process, there are numerous reports of changing rate-limiting processes. These cases will remain intractible for complete treatments by present methods. Such processes can be identified, however, by the tests suggested above so that minimal time is wasted trying to compute kinetic parameters. Even so, there ought to be many processes wherein the change from one rate-limiting step to the next is clearly-enough defined that the steps may be treatable separately. This can occur when Step 1 goes nearly enough to completion to enable satisfactory data collection and computations and Step 2 continues beyond the time that Step 1 is virtually complete. On the other hand, a reaction may appear to accelerate as initial reaction removes some barrier; this kind of behavior (change of mechanism) impairs the validity of any calculations that attempt to treat the overall process, so occurrences must be detected. Another kind of overall process that will provide a serious problem is that in which there are several kinds of bonds being broken concurrently. It should be evident both that any rate measuring the overall process cannot be resolved well enough to describe any one of the individual processes and that any overall calculated temperature dependence has no relation to a real activation energy.

ARGUMENTS FOR SEPARATION INTO HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

Advancement of Knowledge. The major reason for separation of treatments of processes is to determine whether or not there are processes that survive the tests, that is, continue to be describable by homogeneous kinetics and to yield reproducible kinetic parameters from laboratory to laboratory and instrument to instrument. Determination of the status of a given process should lead to more-accurate description of that process and an activation energy is constant for a given reaction wherever and by whomever it is carried out.

Tests of Reaction Progress. Tests to determine the continuity of any process are conspicuously absent in the literature, yet the possible tests are simple. Especially when the kinetic model to be ascribed to a process has been chosen only for its closest conformity to a calculated curve, a test should be used to assure the experimenter that the model does indeed describe the process satisfactorily. Two very simple tests are change in sample size by the largest factor that is reasonably convenient and change of the sample geometry or enclosure. Each of these can be performed without even a change of programming. 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. These are tests that ought to be done before even reporting values within one's own organization -- for example for processing planning.

More extensive 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 include firm evidence that the chosen model is the correct and only model. One very useful test comprises using the numeric values of the kinetic parameters calculated from the assumed model to calculate the temperature that would provide, say, 70% reaction overnight with no other change in experimental conditions and, of course, verifying that behavior.

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, but 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 consistent temperatures near 700°C in vacuum, air or carbon dioxide whereas the decomposition of anhydrous calcium oxalate proceeds ca. 500° under a similar range of conditions. There are many varying reports about kinetic models for calcium oxalate -- all using "established" models and none including critical testing. In the organic/polymer field, there are at least some reversible reactions.

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 equation to describe the process precisely.

DISCUSSION

Reaction of Principal Component. The earlier discussion of the energy distribution suggested that a thermal event in a material in dilute (solid) solution may indeed be describable by the generalized Equation (3). Turning to the principal component (matrix), ranges of behavior have been observed, and these 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 valid in that there are many systems -- most inorganic decompositions -- for which Equation (3) is totally without merit and many others -- most polymer and other glassy systems -- for which it is well-established.

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 well-describable by homogeneous kinetics.

These homogeneous-kinetics processes may be limited to relatively low enthalpy changes. 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 for both direct chemical interaction and for free-radical processes. In short, there are reactions of the matrix that are clearly describable by homogeneous kinetics.

CONCLUSIONS

There is very sound reason for believing that the *valid* vs. *invalid* arguments concerning the use of homogeneous kinetics and its generalized equation in describing thermal decompositions of solids are futile; there is adequate reason to believe that they are applicable in some circumstances and not in others. In many reports on specific reactions a determination cannot be made at present because parameters other than the concentration -- but not included in the $f(x,\ldots)$ statement -- may be influencing the rate of the reaction. That is, the true condition may be more complex than a simple dichotomy.

The completeness of the reaction statement can be tested by simple variations in the experimentation. If the reaction statement is complete, there will be no change (beyond experimental error) in the computed kinetic parameters. If there is a change, the source should be sought and its influence ascertained. *Authors should make these tests to save time and to avoid later criticism of their reports*; editors/reviewers should require the tests for scientific clarity.