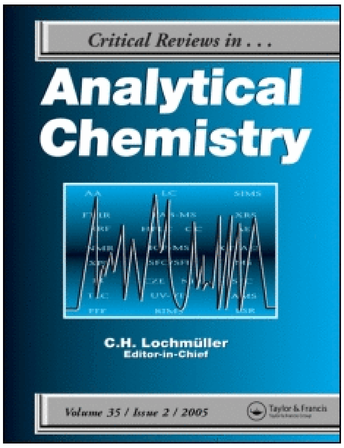

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KINETIC INVESTIGATIONS BY TECHNIQUES OF THERMAL ANALYSIS

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PREAMBLE

The kinetics of thermal decompositions has been studied by dynamic thermoanalytical techniques because such techniques seemed appropriate and economical in time in spite of the obvious problems.

The very extensive investment of time and equipment required for exacting studies of decomposition kinetics has made dynamic methods appear very attractive; one or a few weight loss curves, each requiring several hours, followed with detailed computations, require less total effort and time than a complete series of isothermal, isobaric experiments.

The concepts that are well established in homogeneous reactions have been adopted with little criticism by many practitioners, even though they may be abhorred by more orthodox solid-state kineticists. One purpose of this paper is to point out the deficiencies in extant widely held views and to assess what strengths they have. To that end some sections will assume a dogma and argue the consequences, while another section may comprise a determined attack upon that same tenet. In no case should the author's firm support be assumed.

Readers experienced in solid-state kinetics studies should bear in mind that this critique is directed mainly to the user of dynamic thermoanalytical techniques. The many studies of kinetics of particular reactions by nondynamic methods are not reviewed comprehensively herein, even though a number of such studies are cited in relation to thermoanalytical experimentation.

Authors have frequently taken the mathematical methods of homogeneous reaction kinetics and applied them uncritically to systems that cannot possibly be described as homogeneous, sometimes making assumptions which find no support in physical reality. Other workers, encouraged by the apparent acceptance of the methods by the scientific community, have adopted the same, or slightly changed, mathematics to describe new reactions.

The criticisms raised by a few writers have not yet stemmed the tide, although these criticisms appear to be increasingly effective. The errors of yesterday are not buried, however. They are preserved in the scientific literature for neophytes to discover and reuse. A larger criticism is particularly useful at this time when literature searches can move forward in time with respect to the article. It is now possible to learn the evaluations of later workers by a citations search.

This article is written as an aid to workers in kinetics and/or thermal analysis, with the expectation that discovery of evaluations of a technique by other workers will guide the design of experiments or the method of processing the data.

The criticisms raised herein will hopefully serve to alert the writer to possible objections by reviewers if he follows the well-trodden paths, but it may also serve as a check list for reviewers.

For whatever comfort it may bring the writers cited, this author freely admits that he does not have a set of positive truths. Interpretation of kinetic data by any method is seldom easy, and many workers hope that treatment can be placed upon a "solid" footing. This criticism is by no means intended to stifle new work, but it is intended as an aid in avoiding fruitless endeavor.

The special problems of decomposing polymers are not covered in this work. They provide some simplifications and some complications, but in the inorganic chemical and mineral fields more familiar to the author there are already enough features needing clarification. The heat transfer and measurement problems are similar and the activation energy discussion is equally appropriate. However, the discussion of depolymerizations, scissions, fragmentations, and the very high probability of concurrent processes would be inappropriate here.

The format herein is necessarily irregular. The several effects that influence behavior are not easily separated. Appropriate articles are cited to make the important points, but this review is by no means exhaustive. It is intended to clarify uncertainties rather than to assemble data.

Finally, a number of caveats based upon the cited observations will provide the reader with a starting point for action or argument, and discussion of a more general form of rate equation suggests a tool for discerning and possibly separating different mechanisms.

INTRODUCTION

The methods of thermal analysis under consideration are those in which the temperature of the sample is systematically changed while the weight, a temperature difference, or some other parameter is measured as a function of the temperature or time. The principal ones of these are thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). These abbreviations are those adopted by the International Confederation for Thermal Analysis and its nomenclature is used throughout.

TG has the distinct advantage of providing very good numerical or analog information on the weight of the sample, but usually much less satisfactory data on the temperature of the sample. It has a further disadvantage; the sample is ordinarily rather isolated from the heat source, so it may not follow the temperature program very well.

DTA is the most adaptable technique for thermoanalytical measurements in general, but many of the sample configurations having great utility for other purposes have little value for kinetics. The sample temperature is easier to measure and program than in the other techniques.

DSC has the advantage of providing better information on energy consumption than DTA at the price of poorer knowledge of the sample temperature.

These general criticisms are true for most apparatus. With sufficient investment of time and money, most of these criticisms can be overcome.

The quantities to be determined as part of a kinetics study are the rate of the reaction, the specific rate constant, and the activation energy. Very frequently forgotten but nonetheless real is the heat of reaction.

The search for accurate descriptions of real chemical processes is hampered to some extent by a pair of related semantic-philosophic conditioned thought patterns. The one of most concern here is the concept that *reactions obey equations.* Upon examination of the statement it is obvious nonsense; the inanimate material neither knows nor understands equations. While most authors are well aware of this, some are not, and it is sometimes painfully evident that data have been pushed and pulled into a form which conforms to a known equation or the authors' predilection.

The very human tendency to search the literature only until a reference can be found to justify a conclusion tends to propagate errors so that deviations from more common behavior become classified according to superficial resemblance to something previously reported. This permits the strengthening of allegiances to first-order kinetics, Bessel functions, etc., even though the greatest excitement in scientific research is study of the unusual phenomenon rather than fitting a reaction to an equation covering 20 to 40% of the process. There is need to classify in order to bring into being an *ordered* knowledge, a science, but whatever order exists will be more easily recognized if the scientist does not unconsciously or subconsciously require that everything must fit the pattern.

The second effect of conditioned thinking is the concept that *experiment must be in accord with theory.* This is almost a paraphrase of the other, but a more general statement. If the concept was correct, of course, the lack of affirmation in the Schrödinger equation would deny the existence of nuclear quadrupole resonance, or an isotope effect in atomic absorption spectrometry. Again, it is by study of deviations from ordered knowledge that science advances. *Theory must describe experiment* and if it does not, but the experiment is valid, the theory must be changed.

In practice, it is reasonable and proper to test data against known equations describing other systems or models. It is unreasonable and improper to ignore deviations in order to be able to set down a value for the activation energy or order of reaction. Just as theory must agree with experiment, the equation must describe the reaction.

COMMONLY USED MODELS OF SOLID-STATE REACTIONS

Before entering into the critique of the thermoanalytical determinations of kinetic parameters, it is appropriate to look at some of the simpler models used to describe the kinetics of thermal decompositions. Reactions which occur along well-defined boundaries may be of several types, depending on the anisotropy of the material.

An isotropic material may react uniformly beginning at the surface, the reaction front moving inward. If the reaction front moves at a constant rate, the observed rate depends upon the shape of the particle or entire sample. For a sphere, the reaction is describable by

$$kt = 1 - (1 - \alpha)^{1/3}, \quad (1)$$

while for a cylinder,

$$kt = 1 - (1 - \alpha)^{1/2}, \quad (2)$$

or a single face

$$kt = \alpha, \quad (3)$$

where α is the fraction reacted at time t.

Equation 2 would also hold for circular platelets or layers reacting inward from the edge.

These topochemical descriptions do not cover all cases. Nucleation of a reaction need not occur on a surface or at the edge of the whole sample. For reactions occurring uniformly in all parts of the sample,

$$kt = f(\alpha)^n, \quad (4)$$

but for nucleation of limited numbers followed by growth of the nuclei first into stable particles and then into joined particles, several equations have been developed for various cases. The most popular of these is the Avrami-Erofeev equation

$$kt^n = \ln (1 - \alpha), \quad (5)$$

where n is an empirically determined constant.

The equations developed for specific limited parts of the whole decomposition process are not being examined at this point because they are not in common use in interpreting thermoanalytical data. A greater listing is given by Šesták and Berggren in their examination of similarities of models.

The considerable number of models may have been developed to largely describe real cases, or many may have been developed simply because the experimental data did not fit any single model already developed. The differences are not very great in several cases. It is probable that in several cases the difference between equations is less than the experimental error of the data.

An even greater hazard, though, is that concurrent processes blur the resemblance of the whole effect to either (or any) single process. Eckhardt and Flanagan have pointed out that close fit of a chosen equation does not insure that the mechanism described by the equation is the correct one. They showed that a contracting parallelopiped or a contracting sphere model fit the experimental data about as well as the correct (from optical evidence) model, a contracting parallelogram. The data may tend to resemble the former because of a slow growth parallel to the *a* axis, since an opacity did develop, even though the major contribution was movement of interfaces inward toward the *a* axis.

Models are useful for picturization of a process and for developing mathematics describing a possible behavior. Extensive reliance on a single model or *a priori* confidence that any reaction will conform to a single model is unwise.

CHEMICAL REACTION RATES

The rates of many chemical reactions are high enough so that some other process limits the observed rate of reaction under the conditions of the experiment. If the experiment is designed to avoid other limitations and the observed rate is measurably slow, or if the effect of other parameters is known and the observed rate is less than the calculated rate (Hills, 1967), a chemical rate may be inferred. But until the other probable limitations have been taken into account, attribution of a measurable time of reaction to a chemical rate is untenable. There are already many accounts in the literature ascribing chemical rate constants to very rapid reactions which cannot proceed because of a deficiency of heat or a superabundance of reaction product.

Rates of reaction in homogeneous systems have been studied long and intensively enough to enable reasonable descriptions of many reactions in solution or the vapor phase. Even here, exceptions must be made to the term *homogeneous*; some reactions only take place at a wall, presumably because special orientations are required, or in a catalyst for similar reasons.

Now contrast the homogeneous solution with a typical solid material approaching a temperature at which it can react at a measurable rate. The solution can be stirred to attain thermal and chemical homogeneity; the solid not only cannot be stirred to attain thermal homogeneity, but also the large-scale chemical homogeneity cannot be used as a basis for assuming short-range chemical homogeneity, and especially it is no basis for assuming short-range homogeneity of free energy. The existence of edges, grain boundaries, lattice vacancies, lattice impurities, and such tends to make some regions of a particle more reactive than others. Many of these kinds of disorders are directly attributable to the manner of preparation of the sample, rather than to the intrinsic reactivity of the material.

But now let the material begin to react. Assuming it is being heated by way of the container or support, reaction of any material not in contact with the wall will require heat transferred through the material between it and the wall. Transfer of heat requires a temperature gradient. If the reaction is *very* slow, the temperature gradient may indeed be negligible, but if the reaction is proceeding at a moderate rate the material nearer the wall may well be consuming far more heat than it passes on. If any substantial number of particles are involved, it is plain that only the very reactive sites on the more distant (from the wall) particles can react before much less reactive sites on particles nearer the wall have reacted.

It follows that at any but *extremely low* rates of reaction (or extremely low heat of reaction), the reaction cannot proceed at even nearly the same rate in all parts of the specimen. Even more clearly, "isothermal" studies will already be based on questionable assumptions, so "nonisothermal kinetics" at moderate rates of reaction represents substantial quesswork.

The argument may be advanced that one may use an extremely thin layer of sample to avoid the inhomogeneity in temperature. This is quite true, and if the preparation of the thin layer does not cause additional disturbance of the crystal lattice, a nearer approach to the chemical rate may be attained. Whether or not valid data will be obtained depends largely on the kind of measurement made. Measuring the temperature of the supporting surface would be risky; measurement of the mass would require very special effort or expense to be sure the temperature is known accurately; measurement of evolved gas sharply limits the use of controlled atmospheres. The present author has already discussed these problems at length (Garn, 1965b).

SPECIFIC RATE CONSTANTS

In the study of solid-state reaction kinetics it is customary to obtain the data by measuring either the amount of a product or the amount of a reactant remaining and converting the measured quantity to a fraction of the sample. Then the question arises: How does the fraction remaining affect the instantaneous rate of reaction?

The general method of answering the question is to test the data successively in various equations, trying one after another until a constant value (within acceptable limits) is found for a term k in the equation selected. The model described by the equation is then assumed to provide the correct description of the reaction under investigation.

Let us look back at the normal development of theory in physical sciences. From observation of phenomena or behavior, a hypothesis is developed and examined. If it provides a satisfactory description the hypothesis becomes a *pro tempore* theory. As more knowledge comes into being, it is probable that some exceptions to the extant theory are found. If these cannot be explained, a new theory or an extension of the old is developed. The superlative example of this development is the collection of name-brand effects along a carbon chain as various groups affect not only the carbons to which they are attached but also those two, three, or four units down the chain. Some of these effects have to be described in terms almost directly opposed to other effects. The several effects are explained on the bases of certain properties of the various groups. This is not being critical in the personal sense of the term. The deviations exist. There is a reason for each. We do not yet have an adequate unified theory that will explain all behaviors. It would be supreme conceit to believe we were substantially better off in solid-state kinetics.

The simplest model that can be reasonably ascribed to solid-state reactions is the zero-order reaction,

$$\frac{d\alpha}{dt} = -k_T. \tag{6}$$

This states that the reaction proceeds at some constant rate, k_T, characteristic of the temperature. The obvious model is a reaction being limited by heat transfer or, in some geometries, by mass transfer (reactant or product).

The most common model into which solid-state decompositions are molded is the first-order reaction,

$$\frac{d\alpha}{dt} = -k_T\alpha. \tag{7}$$

This states that the reaction proceeds at a rate proportional to the fraction of reactant still unreacted, the proportionality constant being specified for each temperature. To be valid, this is necessarily a homogeneous reaction; that is, both the rate and composition are the same throughout the specimen. The unquestioned example of a first-order reaction is radioactive decay. Reactions of higher order are difficult to justify by any reasonable model.

ACTIVATION ENERGY

The activation energy for a solid decomposition reaction has an esoteric definition, a prosaic means of determination, and generally a very questionable meaning. Classically (that is, from homogeneous kinetic theory) it is the free energy needed to raise the reactant from its previous state to an "activated" state (Figure 1), from which it will quickly fall to either the "reactant" or "product" state without regard for the state from which it came. The rate of reaction of this activated state is so high, *kT/h*, that it is not the limiting step in ordinary cases. The activation energy is defined in terms of the specific reaction rate constant (or k_T in terms of the activation energy) as

$$k_T = Ae^{-\frac{E}{RT}} \qquad (8)$$

$$\text{So } \ln k_T = \ln A - \frac{E}{RT} \qquad (9)$$

$$\text{and } \frac{d \ln k_T}{d\, 1/T} = -\frac{E}{R}\,, \qquad (10)$$

a favorite starting point in treatment of thermal analysis data. This states that if $\ln k_T$ is plotted against $1/T$, the slope is $-E/R$. When applied to the entire decomposition this requires some assumptions that simply cannot stand up under rigorous examination; one is that the rate expression chosen is valid through the entire reaction; another is that the rate "constant" follows the expression derived and verified for homogeneous reactions, and a third is that the rate expression chosen is the correct one (assuming there is a correct *one*).

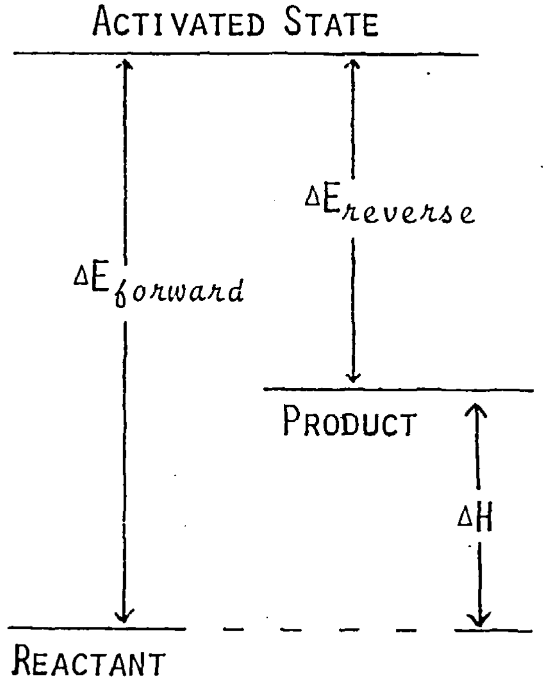


FIGURE 1. Energy level diagram for a hypothetical simple reaction.

The first assumption can be shown to be invalid in some cases, but the incomplete data or descriptions prevent a sure test for every case. Hulbert has shown that the reaction between magnesium sulfate and chromium (III) oxide follows substantially different kinetics at various stages of the reaction. Figure 2 shows the several stages which, if smoothed carelessly, could be described by a nucleation and growth expression. Study of the dehydroxylation of kaolin in this author's laboratory shows that the reaction model does indeed change with pressure, following the mathematics of the nucleation and growth model at higher water vapor pressures, but approaching first-order kinetics (m=1.00) at lower pressures. Many other examples can be cited in which there is some effect that disturbs the simple relationship. Generally, though, some other deficiency in the experiment contributes, so the invalidity of this assumption is no more proven than is the validity.

The validity of the homogeneous rate constant expression can be questioned on a number of grounds, the principal one being that we do *not* have a homogeneous sample. The edges, displacements of various kinds, vacancies, and impurities all deform the energy distribution that could be expected of a homogeneous sample. These variations from the normal lattice sites are all *higher* in energy, hence tend to be "activated" first. If the defect is such that reaction propagates the defect,

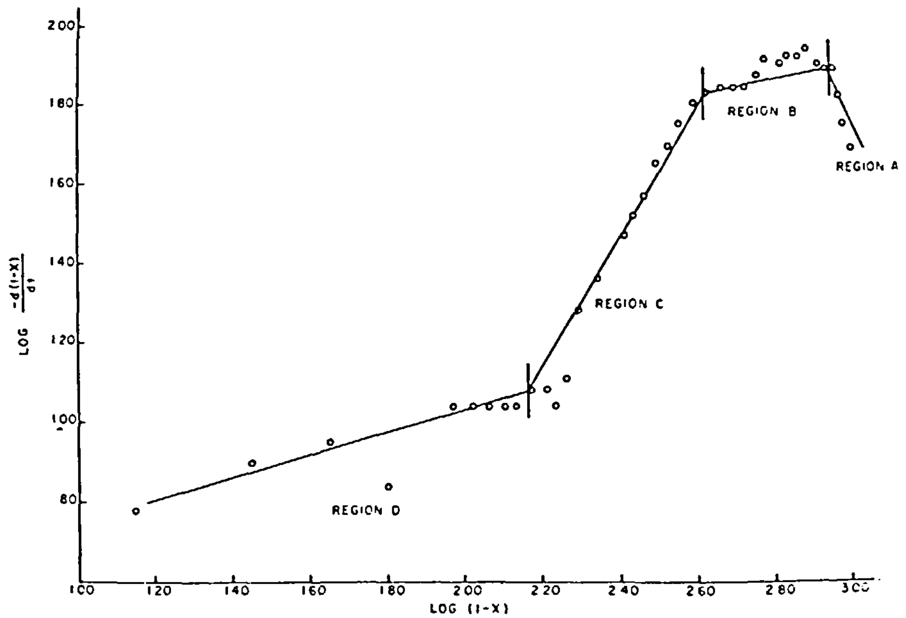


FIGURE 2. Van't Hoff analysis for the reaction $MgSO_4 + Cr_2O_3 \rightarrow MgCr_2O_4 + SO_3\uparrow$ at 950°C (1 g specimen pressed at 8,000 psi). (Hulbert, from Schwenker and Garn.)

a substantial portion of the reaction will arise from a small fraction of the specimen. The properties and behavior of defect structures and "active sites" or "active regions" are too well known to allow implicit faith in any assumption of homogeneity of solid samples or computations based upon homogeneity.

The similarity between some of the forms of rate equations should not be surprising. There are probably gradations in behavior so that reactions can be found that have some properties of both of any pair of models.

In principle, the thermodynamic enthalpy change should represent a lower limit to the calculated activation energy (Figure 1) and should equal the difference between the activation energies of the forward and reverse reactions. For this to be true, the same activated state must be reached from either side. It is conceivable that different activated states exist, so that $\Delta E_{reverse} + \Delta H \neq \Delta E_{forward}$.

Warnings that the activation energy is a questionable concept have appeared in the literature many times. The question remains unresolved largely because one can determine a quantity in the same manner as in homogeneous kinetics and call it the activation energy. Hauffe suggested that no real physical meaning could be ascribed to the activation energy without knowledge of the mechanism of the reaction. Ingraham raised the question of whether its determination had either basis or value other than as the temperature coefficient of the rate constant. Gomes points out that there is no reason to expect k to increase with temperature exponentially in all solid-state reactions.

SUCCESSIVE OR PARALLEL REACTIONS

The preceding discussion has assumed a single mechanism. Some reactions proceed by competing mechanisms whose relative contribution may vary with temperature, pressure, or degree of reaction. Each of these, if separable, could be described by its own specific rate constant, activation energy, and frequency factor. In many cases, they will not be separable.

There may be such a smooth variation in relative importance that the values of the kinetic parameters show a quite uninformative trend, rather than discernible discontinuities. These are not amenable to simplistic or even simple kinetics treatments.

The real value of kinetics treatments will be to discern these variations. To learn that a reaction is describable by the nucleation-and-growth model from 15 to 40% reaction under certain conditions is not very helpful. Several questions arise:

What is happening in the early stages?

Would that early stage process actually go to completion in an isothermal experiment?

Does the changing pressure at the reaction site affect the actual rate?

How much smoothing of data was needed to set the stated limits? That is, was there a substantial contribution from another process at either of the stated limits?

The answers to these questions will help determine whether or not the course of the reaction should be described by a single set of parameters, or whether the first and last portions of the plot should be investigated further.

There is no fundamental reason to describe a complete decomposition reaction by a single set of parameters. Separate *k*'s with their different temperature dependences are not only justified but often will provide a far superior description of the reaction.

An especially important precaution in calculating activation energies for a whole reaction is assurance that the same reaction is taking place throughout the process. In the case of magnesium oxalate, two gaseous products are released, $MgC_2O_4 \rightarrow MgO + CO + CO_2$. Wiedemann et al. and Ponec and Daneš assumed a single reaction. This is implicit in their determination of activation energies shown in Figure 3. But the similarity of the right-hand ends of the plots should not be overlooked. The rising tendency suggests the possibility of a stepwise process. Certainly other studies of oxalate → oxide reactions show that the process changes. Wang has shown the changing relative amounts of carbon dioxide and carbon monoxide evolved from lanthanum oxalate hydrates prepared by three separate methods. Her data are shown in Figure 4. The present author (1965a) has shown that even the de facto "standard" calcium oxalate does not decompose stoichiometrically in the absence of oxygen which suggests a stepwise process.

THERMODYNAMICS

The general laws of thermodynamics have been developed to describe real systems, although very often using models that are limited in utility to their immediate purposes. The behavior described by thermodynamics will be followed by materials in a DTA or TG furnace, but it is as important to know what thermodynamics does *not* say as what it does say.

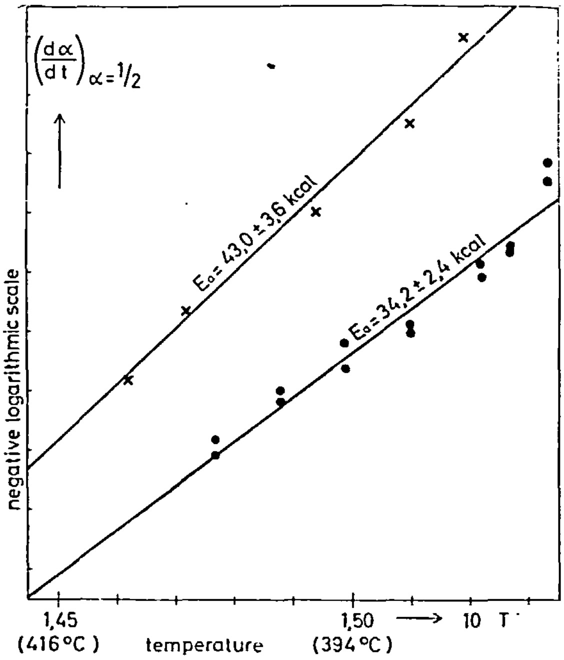


FIGURE 3. Comparison of rates for decomposition of magnesium oxalate at $a = 1/2$ by ± Ponec and Daneš and Wiedemann et al.

Draper and his co-workers recognized the shortcomings of the several methods used in both programmed-temperature and isothermal kinetic studies and, having analyzed the reasons for the deficiencies, they developed a method which purports to be applicable to all *solid → solid + gas* reactions. Draper, however, claims that "the elimination of isotherms and the Arrhenius equation as invalid in solid-state decompositions leaves only thermodynamics and physical properties or the basis for any new theory." He then proceeds to state that "when a sample is exposed to conditions of temperature that will cause it to react, it responds by reacting...... No higher temperature can exist during reaction, for this would mean that the reaction is already over," and "if Δ G becomes at all negative with respect to the reactant, the reaction will have occurred." But thermodynamics does not say this at all. It states only that the reaction can occur, but not that it will occur in either a millisecond or a millenium. To admit the basis for Draper's derivation would

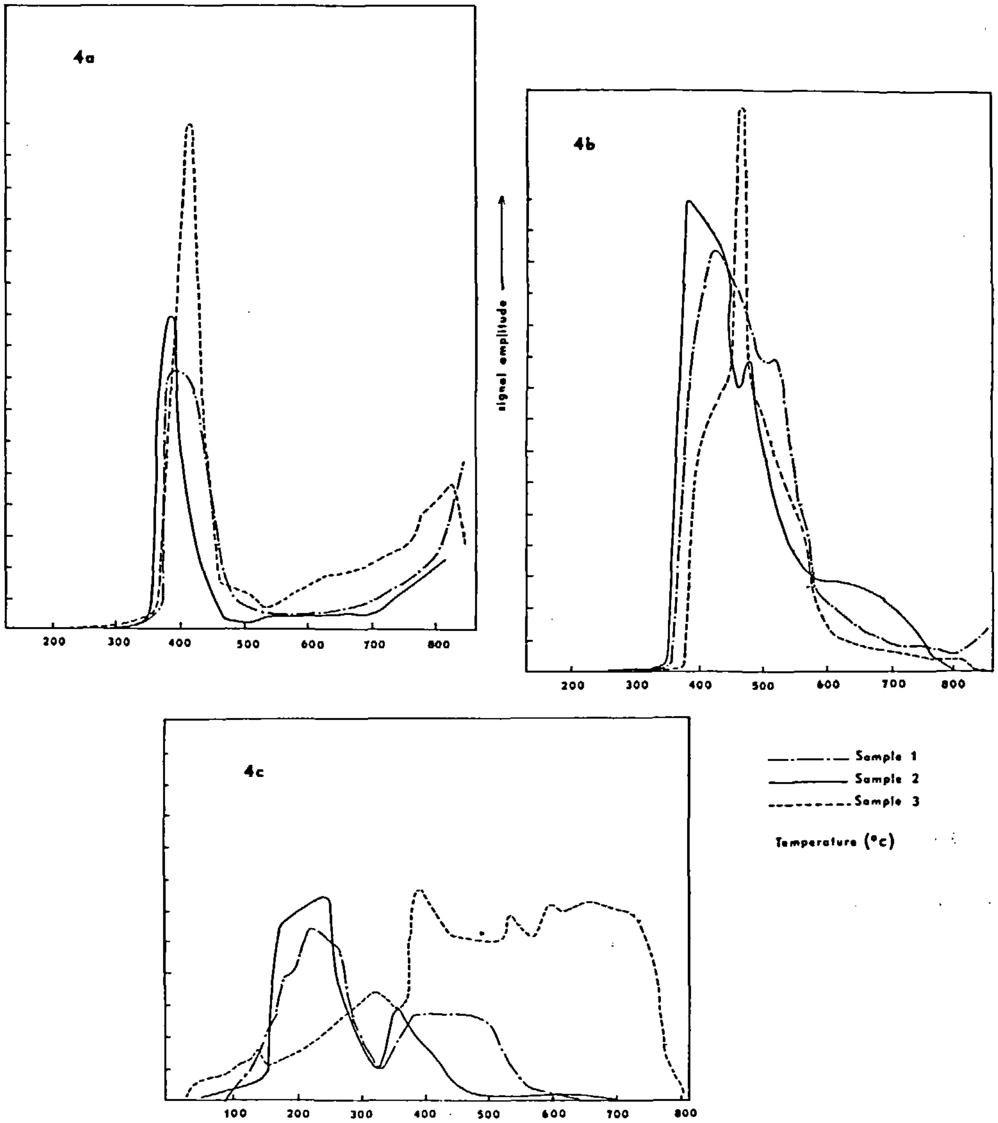


FIGURE 4. Evolved gases as a function of temperature from lanthanum oxalate hydrate prepared by three methods: (a) carbon monoxide, (b) carbon dioxide, and (c) water. The state of hydration determines the crystal structure and hence influences the decomposition. (Wang, using the chromatographic method of Garn and Anthony (1967)).

require the denial of superheating, which can be demonstrated, or supercooling, which can be demonstrated, or any of the multitudes of existing polymorphs which are part of our environment.

The concept of a reaction front has been discussed many times; Smyth (1951) was among the earliest. The present author has pointed out that the apparent kinetics in simple reactions will depend upon the sample geometry. There is no reason to question that many reversible reactions have been incorrectly described in the literature, chemical reaction rates being calculated where some other process limits the reaction.

The conclusions by Draper are no more tenable than those of the most avid kineticist: "No chemical details are needed to predict the complete history and rate of thermal decomposition reactions. The heat transfer and thermal conductivity coefficients of the reaction product, the calorimetric heat of reaction, the sample geometry and a suitable solid-state decomposition equation are sufficient to predict reaction behavior." In effect, the two extremes are reached; the kineticists who ignore thermodynamics are countered by a denial of the reality of kinetics. The real events are not so simple as either side pretends.

Draper also calls for elimination of T_s as a variable, but under ordinary programming the block or other sample holder will experience a change in temperature gradient between it and the furnace wall during the decomposition. The temperature at the surface of the sample will not be a smoothly varying function of time.

There are great differences in the way materials react, and these are involved with the chemistry or the structure of the materials. There are reactions, thermal decompositions included, which are limited in their rates by chemical kinetics, but not as many as the kineticists have calculated for activation energies and rate constants.

VARIATIONS WITHIN THE SAMPLE

During the process of decomposition, changes in the sample or its environment will often influence the course of the reaction. Clarke and Thomas have noted that reactions of the type

$$A_{solid} \rightarrow B_{solid} + C_{gas}$$

do not proceed homogeneously, but are initiated at nucleus-forming sites on the surface. They point out that a complete kinetic description would require knowledge of the rate of formation and the distribution of nuclei, the rate of growth of the nuclei (as a function of direction as well as time), and the size and shape of the parent particles. Consequently, both spatial and time coordinates are needed to describe the rate process completely.

Thomas and Clarke had previously reported on microscopic observations of the dehydration of manganese (II) formate dihydrate, nucleation, and coverage of the [011] faces followed by a constant advance of the reaction interface into the particle perpendicular to the [011] faces.

They find this constant advance to be valid (from their thermogravimetric data) over the fractional decomposition range 0.15 to 0.45, that is, nearly one third of the whole reaction.

They purport to "show that, provided certain readily verifiable conditions are met, meaningful kinetic data can be extracted from TGA (TG)" and subsequently conclude that "thermoanalytical techniques may, in certain conditions, be used to arrive at kinetic data for clearly identifiable steps in thermal decompositions." However, they warn "that these techniques must be used in connection with previous, preferable direct microscopic observations of the reaction."

Their measurements on manganese formate dihydrate comprised thermogravimetric measurements on a 20 mg sample in an electrobalance with a dynamic vacuum of 1 μ torr. With that size sample on that apparatus, the temperature could not be measured directly but must be inferred from the temperature of a thermocouple nearby. At the heating rate of 1° min^{-1}, the error was probably not large; more importantly, it probably varied only slightly over the temperature range studied.

On the other hand, a reaction giving off a gas must lose that gas through the reacted material, so, if this is not a virtually instantaneous process, some pressure of the product gas (water in this case) will exist at the interface. This will tend to slow the reaction, counteracting the tendency toward more rapid reaction as the temperature increases. A pressure term would be needed along with the space and time terms. This term would be somewhat complex, since the particle size would constitute a limit on the diffusion distance. Clarke and Thomas note that "the particle size distribution of the solid is of some significance." The latter half of the reaction is almost certainly influenced by the presence of water quite noticeably, since the water vapor pressure can vary by a factor greater than 10^8.

The qualifications imposed by the authors in effect relegate kinetics by thermogravimetry to the task of providing another curve measuring the same effect the user has already studied in another way.

The method of Coats and Redfern enables calculation of an activation energy and an order of reaction from a TG curve. The values are obtained from a plot of $\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ vs. 1/T. This method may require a number of attempts, using various values of n, to obtain a straight-line plot. The value of n which does yield a straight line is taken to be the order of reaction and the slope is $-E/2.3R$.

The method works from the customary assumption that there is a real, single order of reaction and that the rate constant is completely described by the expression $Ae^{-E/RT}$. Neither condition is met by two of the three steps in the decomposition of calcium oxalate monohydrate which Coats and Redfern use as an example.

The method of Coats and Redfern was examined by Sharp and Wentworth and compared with the methods of Freeman and Carroll and of Achar, Brindley, and Sharp. The method of Achar et al. uses the equation

$$\ln \frac{[d\,\alpha/dt]}{f\,(\alpha)} = \ln \frac{A}{\beta} - \frac{E}{RT}$$

assuming that the sample temperature still increases linearly at rate β during the decomposition, even with an enthalpy change of about 400 cal/g. This is discussed in more detail in a later section.

Sharp and Wentworth reported that in the calcium carbonate decomposition the method of Freeman and Carroll yielded a value for n of +0.55 if 8 data points were used, but −0.01 if 14 points were used. The calculated activation energies were 43 and 36 kcal/mol, respectively. They concluded that the method was unsatisfactory.

On the other hand, the methods of Coats and Redfern and of Achar et al. led to substantially the same results and Sharp and Wentworth found little to choose between them. Both methods require an assumed order of reaction, and for $n = 1/2$ and $n = 2/3$ either method yielded apparent activation energies in the 42 to 48 kcal/mol range for pellets, powders, or mixtures with Al_2O_3 or Fe_2O_3.

The inability to choose between the methods suggests that neither gives any real information about the reaction. Sharp and Wentworth did find that $n = 1/2$ gave better agreement over a wider range of α than did $n = 2/3$ on uncontrolled atmosphere.

The most substantive bit of information is actually the variation in results using the method of Freeman and Carroll. Without arguing for the validity of the calculated values, the fact that n changed so markedly upon extension to a lower α suggests a changing mechanism or substantial change in conditions. In this case, the change was presumably from a condition of easy diffusion of a relatively small amount of carbon dioxide into the surrounding air to a condition in which enough carbon dioxide is within the sample holder to delay this easily reversible reaction. Another change that would certainly take place is the slowing of the temperature rise due to the enthalpy change.

The reason for agreement of the apparent activation energy is discussed later.

Wiedemann, van Tets, and Vaughn have concluded that uniform packing density and thickness are essential to obtain reproducible results in determining activation energies, but the need for reproducible packing implies that something affected by the packing also affects the measured activation energy. That is, if determination of the value of a quantity which is believed to be a function of only two variables requires special effort or precautions not related to either variable, that quantity is dependent upon at least one other variable. In this particular case, it is the atmosphere within the packed sample, and possibly other parameters, that affect the rate, hence the rate constant and, of course, the activation energy.

The basic question to be asked by the experimenter is not so much how to get reproducible results as how to determine what parameters have a direct effect upon the quantity. The temperature measurement and control by Wiedemann et al. are good (Figure 5) so the variable T offers no problem. The quantity k is being treated as an independent variable to ascertain E_a, the activation energy, assuming the Arrhenius equation. This

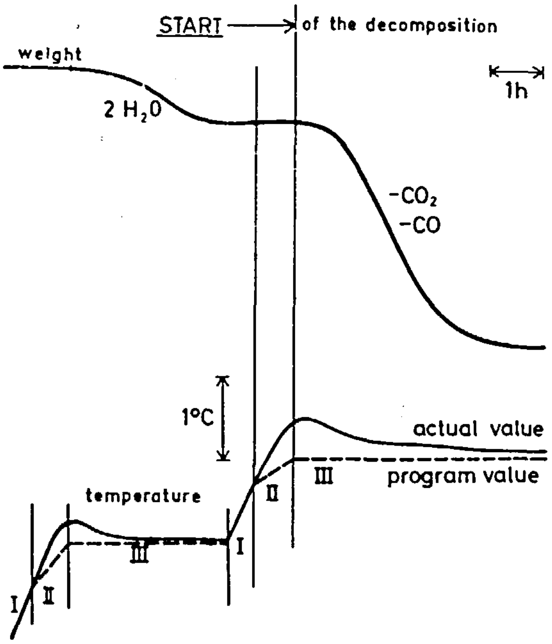


FIGURE 5. The temperature program of Wiedemann et al. for decomposition of magnesium oxalate hydrate at 1 x 10^{-3} torr. The program was set to raise the temperature rapidly to near the decomposition temperature, then approach more slowly and maintain a constant temperature during the decomposition. (Wiedemann et al.)

again leads to the question of the activation energy as a real, fixed quantity, unique for the decomposition of each particular material, needing only to be determined accurately, or whether it is itself a dependent variable having an order of magnitude determined by the enthalpy change for the reaction, but changing with method of preparation, pretreatment, etc.

Assuming an immutable E_a, the defined k is equally fixed if the frequency factor is constant, an implicit assumption by the authors. In practice, the measured k is substantially dependent upon the particle size, packing, and thickness; hence, the equation is incomplete.

TEMPERATURE DEPENDENCE

A reaction increases in velocity as the temperature rises because the reacting system is, in toto, in a higher energy state and hence closer to the activated complex. A larger fraction can reach the activated state. If the activation energy is large, the small increment in energy shown in Figure 6 will not substantially increase the number of activated species, so the rate will not substantially increase. On the other hand, if the activation energy is small, the same increment in energy, as shown in Figure 7, will increase the activated species greatly, so the observed rate increases greatly, too. The low activation energy implies a high temperature coefficient of reaction, or vice versa.

The energy of a total system may well be describable by a single number, but the system does not react as a unit, and that number is not normative for the individual reaction sites. Ordinarily, there is a range of energies, from the lowest energy state of the interior of a perfect crystal through miscellaneous dislocations to the disrupted surface of finely ground particles. As Figure 8 indicates, the increment of energy, E'_A, required for the higher energy sites to reach the activated state is smaller than that required for the perfected crystal. Attempts to describe the system by a single rate constant will be unsuccessful if these higher energy states, E', lie substantially above E and as well populated. The seriousness of this distribution will vary tremendously from system to system for several reasons.

As in the temperature dependence, the effect will be greater with the lower activation energies. The gap is less and the fraction reaching the activated state will be greater.

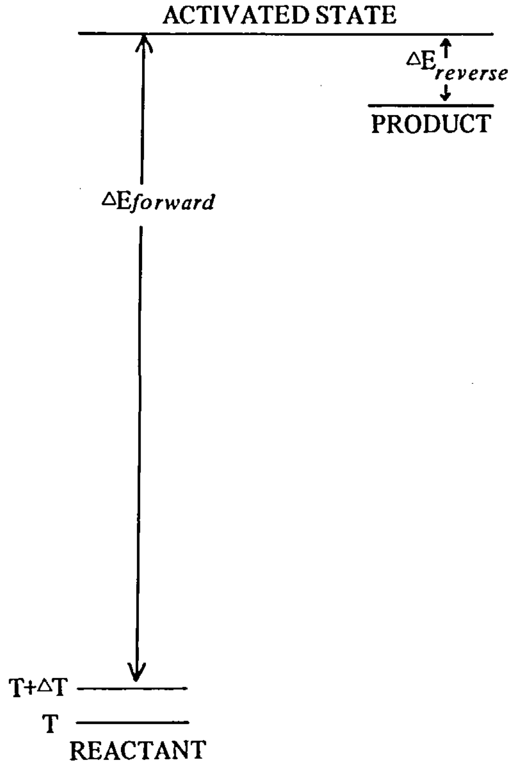


FIGURE 6. Energy level diagram showing large activation energy and an increment of temperature and energy.

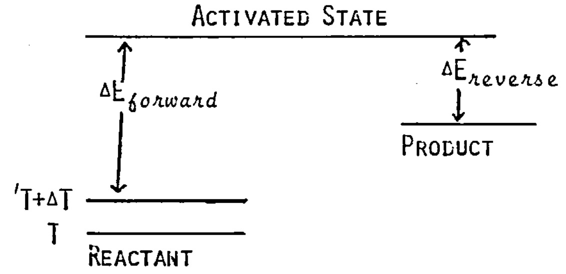


FIGURE 7. Energy level diagram showing small activation energy and an increment of temperature and energy.

The relative ease of reaching the activated state is vitiated somewhat by the possibility of annealing out of the imperfections as suggested in Figure 8. Relatively slow heating, for example, may allow the rearrangement of disturbed surfaces so that the observed rate is significantly different at greater and lesser heating.

Assuming that the variously energized sites follow the customary rules, the observed rate

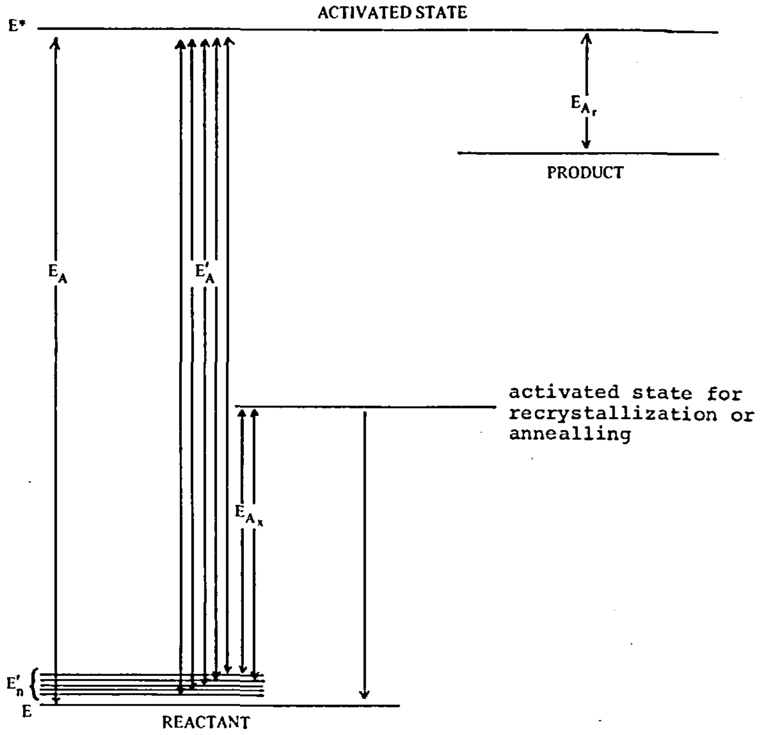


FIGURE 8. Energy level diagram showing several reactant energy levels due to imperfections and an activation energy $E^{\#}$ for annealing.

would tend to decrease as the higher levels were depleted.

One of the apparently simple ways of determining the activation energy was developed by Piloyan et al., who suggested that the activation energy of a chemical reaction can be determined from the initial deviation of a differential thermal analysis peak (Figure 9). They used the assumption, offered earlier by Borchardt (1960), that the early part of the peak is satisfactorily represented by

$$\Delta T = S\frac{d\alpha}{dt}, \qquad (11)$$

where S is the total area of the peak and $d\alpha/dT$ is the rate of the reaction. The assumption is untenable; many effects, especially the need to transport heat and the separation of the point of measurement from the first-reacting material, enter into the structure of the peak (Garn, 1965b and 1969). They substitute this equation into the Arrhenius equation to obtain

$$ln\ T = C - ln\ f(\alpha) - \frac{E}{RT} \qquad (12)$$

and then point out that "it can easily be shown that . . . the change in temperature has a greater effect on ΔT than the change in α . . ." Neglecting ln f(α), they write

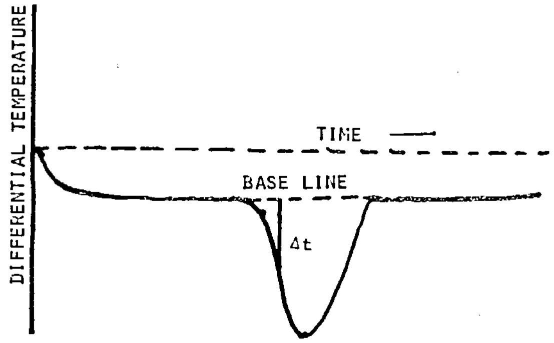


FIGURE 9. Formalized differential thermal curve, showing the various attributes of the thermal effect. (Piloyan et al.)

$$ln\ \Delta T = C - \frac{E}{RT}. \qquad (13)$$

That is to say, the differential temperature is virtually independent of the fraction reacted (between 0.05 and 0.8). This implies that $d\alpha/dt$ must also be independent of *a*, or the basis for his derivation is false. The proper inference is that reactions for which the Piloyan et al. relationship holds are zero order. The reactions cited in support of their calculations are decompositions (some known to be easily reversible) that require substantial heat. Again, the heat supply is the more probable limit on the rate of reaction.

SPECIAL EFFECTS IN VACUUM

It is popularly supposed that if one withdraws gases from a chamber by continuous pumping, the pressure is everywhere equal to the indicated pressure. This is valid, of course, if there is zero leakage and sufficient time has passed to allow a homogeneous distribution of the remaining gases. If there is leakage, or if there is a source of gases, the supposition is invalid. A pressure gradient will exist between the source and the exit (pump). The magnitude of the gradient will depend upon the rate of supply or leakage, which in most cases is itself dependent upon the rate of diffusion from the true source to the interface with the vacuum system.

Take, for example, a deliberate leak through a capillary, such as is used in measuring pumping speeds. The rate of flow from one end of the capillary to another is dependent upon the difference in pressure between the two ends. Restating and assuming a virtually constant low pressure, the rate of flow will depend upon the pressure at the high pressure end. Now if the high pressure end is not an infinite source such as the atmosphere, but is time or temperature dependent, the rate of flow will vary in a manner depending upon both the capillary and the source and, conversely, the pressure drop across the capillary will depend upon the rate of supply of the gas. Moving directly to the system of interest, if a specimen evolving a gas is separated from its surroundings by any barrier to diffusion, the pressure at the reaction site is higher than the observed pressure. The magnitude of this difference depends upon the ease of diffusion through the barrier; hence, if the barrier changes its properties, the pressure drop will change. An obvious change is length, so we may conclude that as a layer of reaction product increases, the pressure at the reaction site increases. This may be of little import in irreversible chemical-rate-controlled decompositions, but can cause serious deviations in reversible processes.

Now take the case of a rapid and reversible decomposition whose reaction product is compact enough to limit diffusion moderately. The slowing of diffusion in turn allows the gaseous product to linger in the vicinity so that the reaction site, even in a high-vacuum environment, sees an appreciable pressure of this gas. The reaction will proceed only at a rate sufficient to keep this internal or interior pressure at the equilibrium value for the temperature of the sample. (Here again, heat transfer may play a critical role.) That is, the reaction is inhibited by its own products, but the amount of inhibition is not constant nor can it be defined readily. The inhibition is not negligible; however, the cross section of the diffusion path is very much smaller than the mean free path of the gas molecules.

Now suppose (arbitrarily) that a pressure drop of 1.0 torr is developed by a sample decomposing at 1% per min at 50% decomposition. If the sample is decomposing against 1 atm pressure, the pressure at the interface is 761 torr.

Since

$$\frac{dp}{dT} = \frac{P\Delta H}{RT^2},\ dT = \frac{RT^2}{\Delta H} \cdot \frac{dp}{P},$$

or

$$\frac{\Delta T}{T^2} = \frac{R}{\Delta H} \cdot \frac{\Delta P}{P}. \tag{14}$$

But $\frac{dp}{P}$ is quite small indeed, so ΔT will also be very small. Now let us evacuate the decomposition chamber to 10 torr, so that $\frac{\Delta P}{P}$ has a quite significant value. Obviously ΔT, possibly without yet being very large, is more significant than in the 1-atm experiment. So continue the evacuation to reach a chamber pressure of 0.01 torr. Quite clearly $\frac{\Delta P}{P}$ is large enough to have a very significant effect upon ΔT. It should also be very apparent that further decrease in the pressure surrounding the sample will have no particular effect except perhaps to maintain the pumping speed; the sample is going to be decomposing under 1.0 torr at the temperature at which this 50% completion is reached, and will not change any further with greater evacuation.

Garner advocates the use of "hard" vacuum because it "plays an essential part in the understanding of the kinetics of the development of dissociation pressures." As the foregoing discussion suggests, it is highly unlikely that the reaction is actually proceeding at the pressure Garner believes because of the difficulty of moving the dissociation product gases from the reaction site to the vacuum chamber. It is much more likely that the reaction is actually proceeding at a pressure which is substantially above that of the vacuum chamber and is neither known nor controllable. This means that the decomposition kinetics as learned in hard vacuum may have little meaning. This is particularly true for stepwise reactions.

The high vacuum also decreases the temperature required for measurably fast reaction, but sometimes at the cost of changing the reaction products. The variation in metakaolinite with pressure of water vapor is certainly well established. Vacuum dehydroxylation leads to a metastable state which persists to near 1,000°C (Figure 10), then rearranges sharply. In comparison, the material formed under several atmospheres rearranges less sharply at a lower temperature. This metastable state is due to persistence of the kaolinite structure after loss of water.

In dehydration of crystalline hydrates at much lower temperatures a different problem arises. The removal of water under vacuum may lead to an amorphous state because there is not enough thermal energy to enable rearrangement during the time span of the experiment. The amorphous state may persist indefinitely or, as in the cases of zinc sulfate heptahydrate (Figure 11) or copper sulfate pentahydrate, rearrange to the crystalline state. The lower the temperature of dehydration the more stable the amorphous residue.

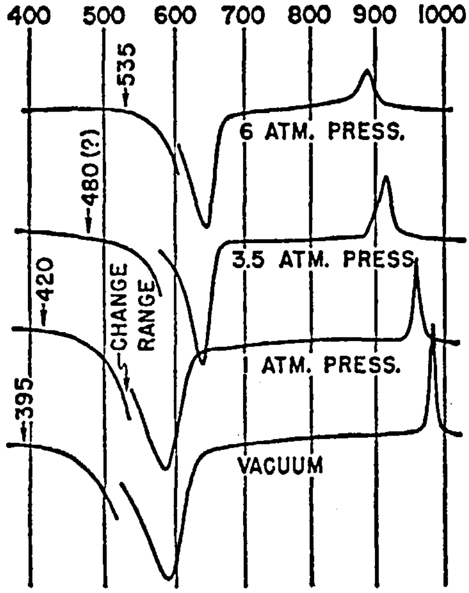


FIGURE 10. DTA curves of kaolinite under different pressures. (Stone and Rowland.) The fact that the water vapor pressure must reach different levels in the several runs leads to a change in environment during dehydroxylation sufficient to affect the exothermic reaction substantially.

In the case of hydrates, the overlapping of reactions can be another source of uncertainty. Copper sulfate pentahydrate decomposes first to the trihydrate if the temperature and pressure lie within its stability range. At quite low pressures, the trihydrate does not form in measurable quantities, but there is a variation in the excess energy of the amorphous state with conditions of dehydration. Frost et al. dehydrated the pentahydrate under varying "water vapor pressures" and found (Figure 12) a decrease, a minimum at 1.4 mm, and a subsequent new decrease in excess energy. The parameter they report as water vapor pressure is actually taken from a manometer reading across a leak and hence a measure of the pumping speed. The pressure at the particle surface is not known very well, and certainly the pressure at the reaction interface is not well known. The combination of temperature (45°C) and pumping speed apparently provides conditions favoring transient existence of the trihydrate. The temperature of the oil bath is the measured temperature and the sample is separated from this by two layers of glass in poor contact. Some very real but unknown amount of self-cooling is inevitable.

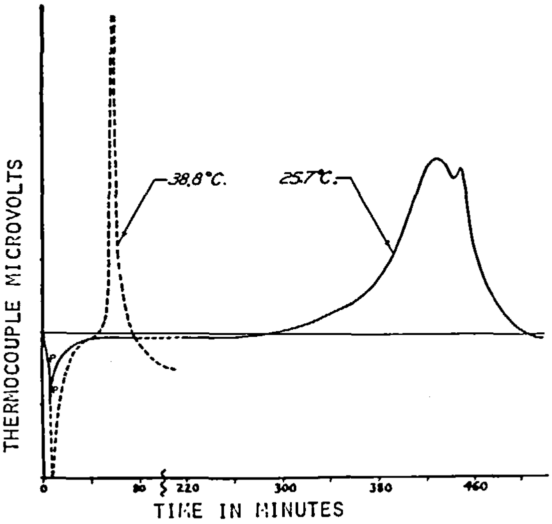


FIGURE 11. Thermal effect following the low pressu dehydration of zinc sulphate heptahydrate at two temperatures. (Frost et al.)

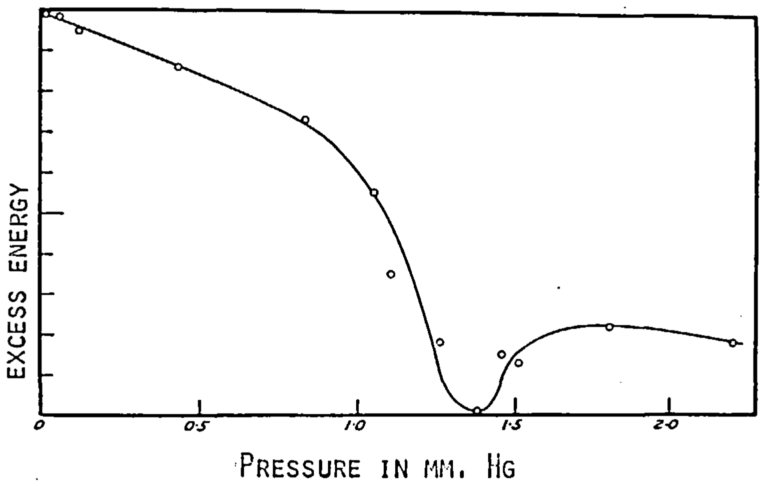


FIGURE 12: Dependence of formation of energy-rich amorphous product on water vapor pressure in reaction zone ($CuSO_4 \cdot 5H_2O$). (Frost et al.)

NONISOTHERMAL HOMOGENEOUS REACTIONS

Borchardt and Daniels studied the decomposition of benzenediazonium chloride (0.4 *M* in water) and derived an expression relating the rate constant to several parameters of the DTA peak. Since it has often been cited in support or defense of other calculations, its validity must be examined. Their derivation was based upon a high degree of homogeneity of temperature. This was achieved by stirring not only the sample and reference solutions, but also the bath (Figure 13). Note that Borchardt and Daniels were well aware that the need to assume homogeneity limited the calculations to reactions in solution.

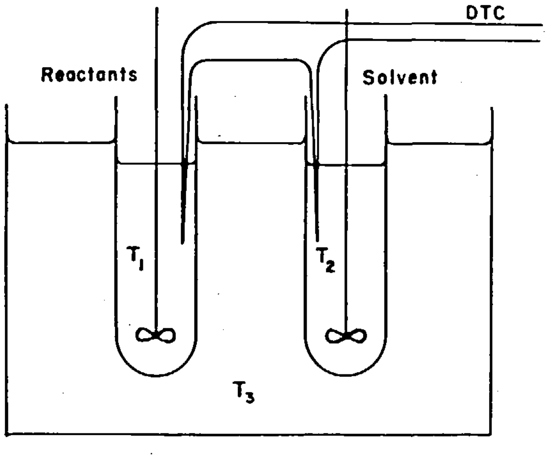


FIGURE 13. DTA apparatus for obtaining kinetic data for reactions occurring in solution. (Borchardt and Daniels.)

The assembly becomes, in effect, two specimens isolated from a heat sink by thin layers of poorly conducting material, glass. The only substantial temperature gradients are set up across that layer. This condition validates their heat balance equations, on the sample side

$$Cp_s \, dT_1 = dH + K_s (T_3 - T_1) dt \tag{15}$$

and for the reference,

$$Cp_r \, dT_2 = K_r (T_3 - T_2) dt. \tag{16}$$

By using identical cells filled and immersed to the same level, they could assume with confidence that $K_r = K_s$ and could simply be called *K*.

But to simplify further, they assumed that a volume of their reacting material at 0.4 *M* had a heat capacity not appreciably different from that of the pure solvent. At 0.4 *M* their solution is about 1 mol % reactant, but their reactant is ionic while some products are not, so the assumption of equal, and unchanging, heat capacities is suspect. But accepting the approximation, Equation 16 may be subtracted from Equation 15 to give

$$dH = C_p d\Delta T + K\Delta T \tag{17}$$

and to express the total heat, the expression is integrated

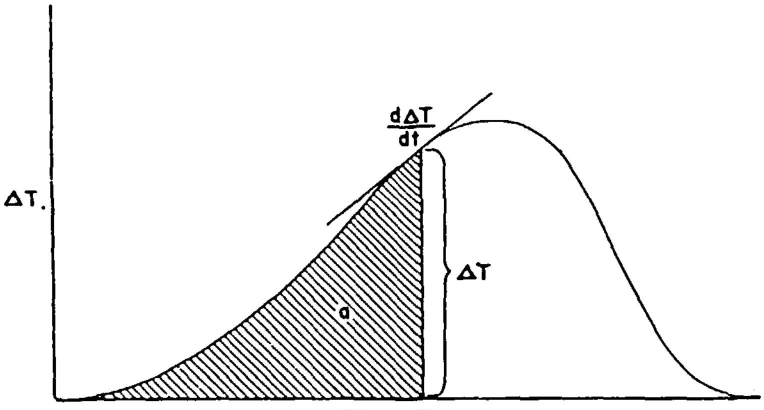


FIGURE 14. DTA curve showing the quantities which are measured in order to evaluate the rate constants for the reaction giving rise to the curve. (Borchardt and Daniels.)

$$_{t=0}\int^{t=\infty} dH = \Delta H = K_0\int^{\infty}\Delta T dt. \quad (18)$$

But if $\Delta T = 0$ before and after the reactions, the integral is the total area under the curve of Figure 14, so that

$$\Delta H = KA. \quad (19)$$

This equation is not unique to this system; it can be derived or found experimentally for solid samples of appropriate geometries too.

The next step, relating the changing concentration to the differential temperature, is acceptable for the conditions of this experiment. For solid systems it is generally not valid because withdrawals of heat from various parts of the sample are not sensed equally by the thermocouple and because adjustments of temperature do not occur instantaneously.

Barshad had shown, many years ago, that a layer of reacting material sandwiched into a column (Figure 15) at different positions with respect to a thermocouple yields DTA peaks different in magnitude, these peaks being larger for material nearer the thermocouple. (Remember, the thermocouple measures directly only its own temperature.)

Borchardt and Daniels next assumed that at any moment *dH* is proportional to *dn*, so

$$dH = KA \cdot \frac{dn}{n_0} \quad (20)$$

follows from Equation 19. Substituting in Equation 17 and looking at infinitesimal time segments *dt*, Borchardt and Daniels state

$$\frac{-dn}{dt} = \frac{n_0}{KA}[C_r\frac{d\Delta T}{dt} + K\Delta T]. \quad (21)$$

The first term within the brackets describes the tendency of the system to respond to change in dn/dt and the second describes the tendency to return to a steady state.

If the number of moles reacted is now evaluated by summing up $-dn/dt$ up to time t,

$$n = n_0 - \int_0^t \left(\frac{-dn}{dt}\right) dt \quad , \quad (22)$$

and substituting for $-dn/dt$,

$$n = n_0 \frac{-n_0}{KA}\left[C_T \int_0^t \frac{dT}{dt} dt + K \int_0^T \Delta T dt\right]$$

$$= n_0 \frac{-n_0}{KA}[C_p\Delta T + Ka] \quad , \quad (23)$$

giving solutions for n and dn/dt (from Equation 21) in terms of quantities measurable from the peak (Figure 14). These may be inserted into the rate of homogeneous reaction equation for a single variable (treating it as a concentration) assuming an invariant exponent, x,

$$k = \frac{-V^{x-1}}{n^x}\cdot\frac{dn}{dt}.$$

The exponent represents the order of reactions, so it may reasonably be applied wherever a true order of reaction can reasonably be assumed.

Substituting from above,

$$k = \left[\frac{KAV}{n_0}\right]^{x-1} \frac{C_p\frac{d\Delta T}{dt} + K\Delta T}{[K(A-a) - C_p\Delta T]^x} \quad (23a)$$

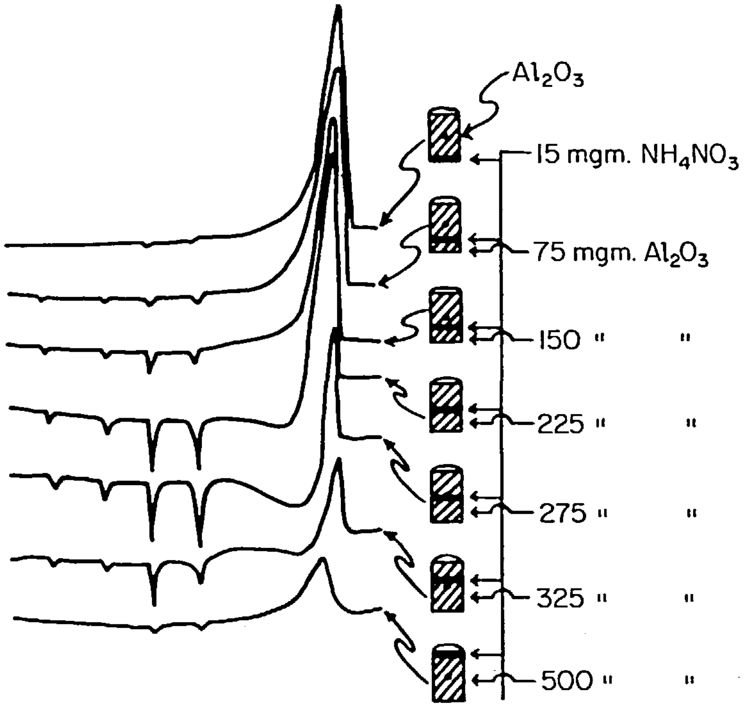


FIGURE 15. DTA curves of 15 mg of NH_4NO_3 placed at different positions with respect to the thermocouples. (Barshad.) The maximum response is obtained when the thermocouple is in contact with the active material.

so that knowledge of the volume and concentration, empirical measurement of K for the cell, measurement of the total area of the individual DTA peak, and several measurements of the instantaneous displacement, ΔT, slope, $d\Delta T/dt$, and fractional area, a, may be used to determine k and x, the rate constant, and the order of reaction, respectively.

The general validity of the mathematical model for the system used is acceptable, but before extending the treatment to solid samples the several approximations and assumptions must be reexamined.

1.*The rate of reaction is very small at the lowest temperature practically obtainable.* This is obviously satisfactory for virtually any solid sample, as are

2.*the reaction goes essentially to completion before the highest obtainable temperature is reached,* and

3.*the reaction must be accompanied by a measurable heat effect.*

But the fourth assumption,

4.*the temperature in the cells is uniform,* is quite invalid for solids. It is not even valid for quiescent liquids. The need to transmit heat in measurable quantities for the "measurable heat effect" implies a temperature gradient. In any sample arrangement in which the temperature of the sample itself is measured, the gradient through the sample itself is an important part of the differential temperature. Sample arrangements in which the temperature of the sample support is the measured quantity have the great deficiency that the relationship of the temperature of the measuring point to the temperature of some point in the sample will vary with the demand for heat. That is, if a particular relationship exists during steady-state heating, but then there is a new and discontinuous demand, the heat flux in the vicinity of the sample will increase *and* change in pattern. At the time when there is the greatest need for a close and constant relationship, it is changing, and changing in a manner which depends both upon the amount of additional heat consumed and the rate at which it is consumed (Garn, 1965b). This latter effect may be due to chemical rate limiting or physical parameters such as thermal conduction.

Borchardt and Daniel's assumption that

5.*heat is transferred to the solutions* (specimens) *by conduction alone* is a function of temperature and cell design. It can be valid, and is valid for their apparatus. Similarly,

6.$K_r = K_s$, and

7.$Cp,_r = Cp,_s$ can be approximated by design of the experiment even though they are not general truths.

The requirement (for the mathematics) that

8.*Cp, K, and ΔH do not vary over the temperature interval where the reaction occurs* is quite untenable for solids. Heat capacities of sample materials will change very substantially while the sample is becoming something else, and the change in ΔH is directly related to the changing heat capacities of reactant and product. The heat transfer coefficients of reactant and product change individually with temperature, and a change in *K* during change in composition must be taken for granted. The expectation that a quantity of an anhydrous salt will take up or transfer heat in the same manner as its hydrated form is quite unrealistic, and the same statement holds for oxalate-carbonate-oxide or any other inorganic systems. A combination which had virtually no change would be quite fortuitous. The only general case for which similarity could be expected is that of depolymerization of a polymer whose monomer units are already more than a few atoms long. Note that Borchardt and Daniel's curve did not return to ΔT=0, even though the active material was diluted 100 to 200 times.

The design of the apparatus can validate the assumption that

9.*no heat is transferred through the thermocouples.* This problem is often overrated. In most designs the thermocouple is in moderately good contact with a heat sink at nearly the same temperature as the sample.

The assumption that

10.*dn is proportional to dH* is reasonable, subject to the limitations set down above, but the extension to a clear relationship to the area under a DTA curve or to the instantaneous ΔT is not valid for solid samples, and would be questionable for unstirred liquids. The thermocouple provides a measure of the temperature of the thermal junction – nothing else. The temperature of the whole sample is generally inferred from this one point. This has persisted in spite of the work of Barshad, who showed quite clearly that the response to a heat effect depended greatly upon the proximity of the material to the thermocouple. The grains in contact with the thermocouple will have a much greater effect than those at a distance. If the thermocouple is not in good contact with the sample itself, the objections given above hold anyway.

For many reactions in solution the concept of a single rate expression can be justified. The individual molecules or ions are interacting mostly with solvent except during reaction. The environment changes but little. So the assumption that

11.*the kinetics of the reaction can be described by a single rate constant* is reasonable, and justified by experience. The extension of this to heterogeneous kinetics is out of the question. Induction periods, the need for reactants to diffuse in or out, and miscellaneous changes in properties of the sample tend to limit the range over which a single effect is rate-controlling. This has been proved time and time again, almost as often as new authors make the same assumption.

The activation energy is a rather clearly defined concept in homogeneous kinetics so the assumption that

12.*the activation energy does not vary with temperature* needs no defense for homogeneous systems. This is closely related to (11) so the same objections apply to extensions to heterogeneous reactions. The experimental data showing variations in activation energy are too numerous to dispute. Most of these variations have other proximate causes, but temperature plays a role in other effects such as diffusion, and other parameters such as pressure affect rates enough that defense or criticism of this assumption is almost irrelevant.

The activation energy and the reason it has any semblance of reproducibility between unlike experiments are discussed in another section.

In spite of all the difficulties and deficiencies, attribution of the general properties of homogeneous reactions became quite popular. Freeman and Carroll (E14) by appropriate differentiation, integration, and division proceed from $k = Z \exp - (E^*/RT)$ where *k* is the *specific rate constant*, *Z* is the *frequency factor*, E^* is the *activation energy*, and *R* is the gas constant, and

$$-\frac{dX}{dt} = kX^x \qquad (24)$$

where *X* is the concentration, mole fraction, or amount of reactant and x is the *order of reaction*, to find

$$\frac{-(E^*/R)\ \Delta(1/T)}{\Delta \ln X} = \frac{\Delta \ln (-dX/dt)}{\Delta \ln X} - x \tag{25}$$

They *conclude*, of course, that a plot of

$$\frac{\Delta(1/T)}{\Delta \log X} \text{ vs } \frac{\Delta \log (-dX/dt)}{\Delta \log X} \tag{26}$$

should result in a straight line with a slope of $\pm E^*/2.3R$ and an intercept of $-x$. Freeman and Carroll proposed to take the necessary data from a single thermogravimetric experiment in which several tenths of a gram of sample was heated at a rate of 10°C/min.

Implicit in their derivation were the assumptions that (1) the *order of reaction is the same throughout the reaction*, (2) the *atmosphere had no effect*, and (3) the *temperature was the same throughout the specimen*. The first of these assumptions is not necessarily correct; the other two are clearly untenable. In their experiment using calcium oxalate monohydrate, not only will the presence of air, rather than water vapor, permit variations in the vapor pressure of water within and about the sample and hence affect the rate of dehydration, but also the air affects the nature of the second reaction. In air, the carbon monoxide moiety of the oxalate ion oxidizes readily to carbon dioxide. The reaction is rapid and sharply exothermic. In Freeman and Carroll's experiment, this reaction took ca. 5 min as compared to the few seconds it would take in a smaller sample. The reason for this is discussed in greater detail elsewhere, but in essence the rate is dependent on the entry of oxygen; however, diffusion of the oxygen inward is inhibited by the nitrogen which diffuses in too but is not consumed and by the carbon dioxide which is being evolved. The third reaction, decomposition of calcium carbonate, is a rapid and reversible reaction. It will proceed at a rate far more dependent on the diffusion outward of the carbon dioxide than on a reaction rate constant. Furthermore, the size of specimen used by Freeman and Carroll is in the range frequently used in older differential thermal analysis apparatuses; at 10°C/min, temperature differences of 20°C or more are easily obtained.

One of the first citations of Freeman and Carroll's derivation of kinetic parameters was by Jacobs, who applied the method to his thermogravimetric data on the dehydroxylation of kaolinite. He carried out the determination in the (then) orthodox uncontrolled atmosphere and hence in an unknown, and nonconstant, water vapor pressure.

From these data, obtained on the submicron fraction from Whitehill pottery clay, Jacobs calculated an activation energy of 37.80 kcal/mol^{-1} and, in agreement with some previous authors, found a reaction order of one.

Jacobs attributed the difference between his value for the activation energy and the 44 to 55 kcal/mol^{-1} previously reported partly to differences in composition and size of particles. Either of these may be expected to have some real effect upon the rate of reaction and its variation with temperature, so this attribution is perfectly reasonable. His partial attribution of disagreement to differences in method suggests, rightly enough, that some error exists in some of the methods. The attribution of real differences in behavior to differences in method, however, is untenable; the differences observed are necessarily deficiencies in experimentation or improper treatment of the data.

The deficiencies in the data treatment of Freeman and Carroll have already been pointed out (although they had not been elucidated at the time of Jacobs' writing); there are deficiencies also in the experimentation reported by Jacobs. Over and above the very clear effect of water vapor, previously noted by Allison, there is a very substantial error in temperature measurement inherent in the experimental procedure. First, the temperature is measured in the *vicinity* of the sample, rather than in the sample. The error is neither known nor constant. At the very time of most concern, the variation is greatest because of the substantial heat of reaction. But even if the temperature of some point in the sample was known, there is no great gain, because the temperature in 2 g of sample resting on a poor thermal conductor, heated at 5° per min, is not going to be uniform, no matter how much the mathematics may require it. And here too, the inhomogeneity is going to be greatest at the time of greatest concern, while heat is being absorbed by the sample in carrying out the reaction.

Using a smaller sample is not necessarily of great benefit; by most techniques the real uncertainty in the *sample* temperature is not diminished.

The general forms of the errors are threefold.

(1) The approximations which are made are inaccurate in the general case claimed. (2) The mathematics fails to take into account the physical attributes of the measuring system, for example, poor thermocouple placement or atmosphere control. (3) The model proposed as a tool in setting up the mathematics is impossible per se because of some requirement contrary to physical reality. One of this third kind is Kissinger's evaluation of peak shapes.

Kissinger developed an expression for the maximum rate of reaction in DTA and, from the variation in the amount decomposed at the temperature corresponding to this maximum rate, proposed the use of a "shape index" to estimate the order of reaction. The assumptions needed to establish the mathematics included uniform reaction throughout the specimen and temperature homogeneity at the same time in spite of the concurrent demand for energy. This is quite untenable; the heat which is needed to carry out the reaction would have to pass through other material which is at the same temperature and is also consuming energy in its own decomposition. A more detailed critique is given in this author's monograph (Garn, 1965b). The shapes (Figure 16) which Kissinger calculates for various orders of reaction are realistic mathematically; that is, they follow from the assumptions. The invalidity of the assumptions removes them from any firm utility in describing real reactions.

The variation in shape can occur from other causes. Wendlandt has shown that markedly different shapes could result from a change in a nonreacting gas. The dehydration peaks for calcium oxalate monohydrate shown in Figure 17 would lead to different conclusions concerning the order of reaction in helium and air, even though the difference is mostly due to the ease of diffusion of both heat and water vapor in helium.

Reed, Weber, and Gottfried also evaluated the equations derived by Kissinger, pointing out from the evidence in their own derivation that Kissinger's model must be in error. Using

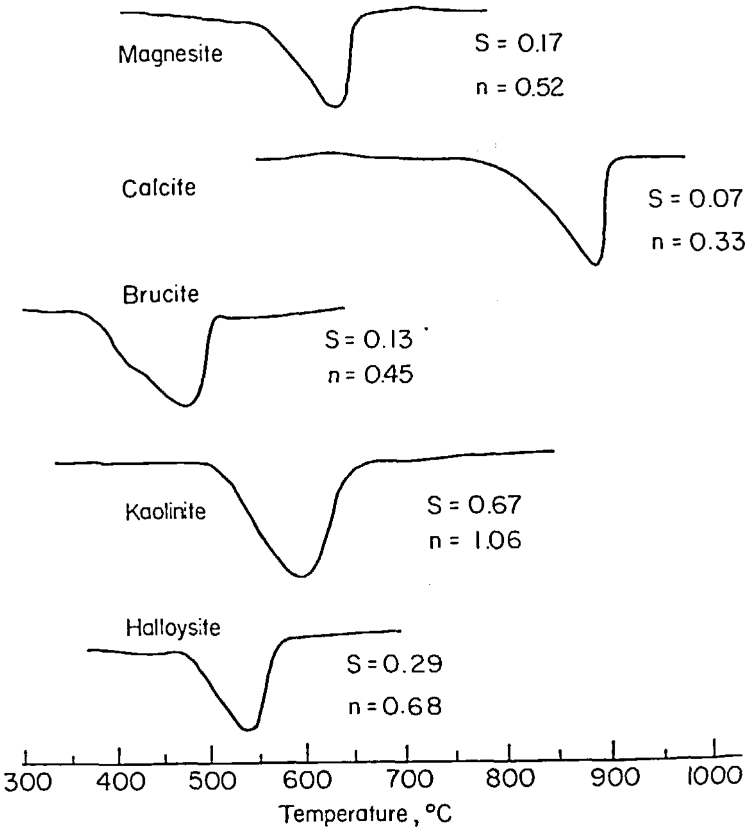


FIGURE 16. Typical differential thermal analysis peaks. (Kissinger.)

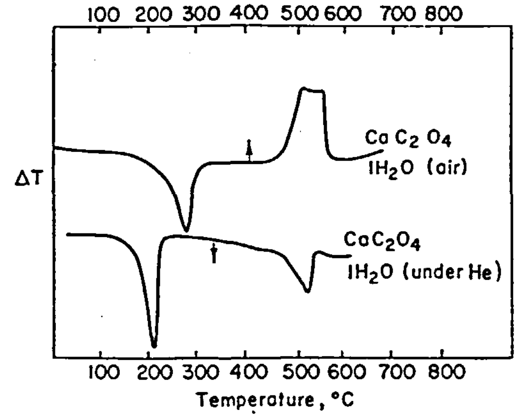


FIGURE 17. Differential thermal analysis curves of calcium oxalate monohydrate. (Wendlandt, from Garn, 1965b.) The peak (200 to 300°C) for the dehydration was used to calculate the activation energy by the method of Borchardt.

Kissinger's equations with their own data, they found E = 16.7 kcal/mol and log A = 10.8 for the decomposition of benzenediazonium chloride, 18.4 compared to 28.7 kcal/mol from the Borchardt-Daniels' method; their data agree very well with those of Borchardt and Daniels and with data obtained by other methods.

The several computed results produced by Reed et al. are instructive in that they show the effects of the several parameters individually, with reasonable assumptions for all others. The detailed figures serve as useful visual aids for consideration of the separate parameters both for evaluating the Reed et al. equations and for general instruction.

The effect of variation in the frequency factor shown in Figure 18 is quite predictable. Once a high enough temperature is reached for any reactant to get to the activated state, there is limitation by a frequency factor as well as by the energy gap. If the frequency factor is extremely high, such as 10^{20}/min, the reaction tends to go quickly, all other things being equal. Noting that the abscissa is an implicit function of time, it is not surprising that a decreasing frequency factor (for example A = 10^{16}/min) should appear to cause the DTA peak to be both spread over a larger temperature interval and displaced to a higher temperature.

Their examination of the effect of variation in activation energy shown in Figure 19 assumed no variation in the total enthalpy change (peak area). Their mathematics requires that absolute temperature of the reaction be effectively proportional to the activation energy for a given set of physical parameters. Typical peak values of $\theta\gamma$ in their work on benzenediazonium chloride are 25 to 31, calculated from their experiments with T_p = 327 and 334°K. The range, too, is proportional to E, so the peak ΔT must diminish proportionately to keep the constant peak area.

Similarly, direct proportionality of the peak temperature to the heat capacity of the cell (assuming constant thermal conductivity) is to be inferred from Figure 20; like the variation with E, it is a necessary consequence of the mathematics.

Variation of the heating rate shown in Figure 21 has quite minor effect upon the temperature of the peak, but this is to be expected for two reasons. The relatively high frequency factor puts some number of molecules into the activated state and the mathematics calls for this number to be independent of temperature; the time dependence of the number which might react is reflected in an

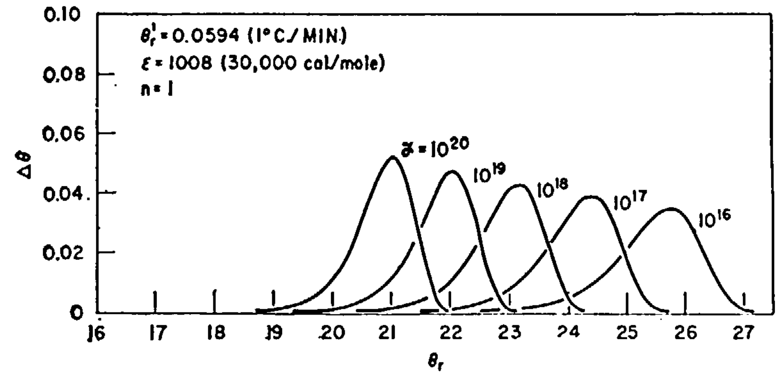


FIGURE 18. Variation of calculated peak shape and temperature with frequency factor. (Reed et al.)

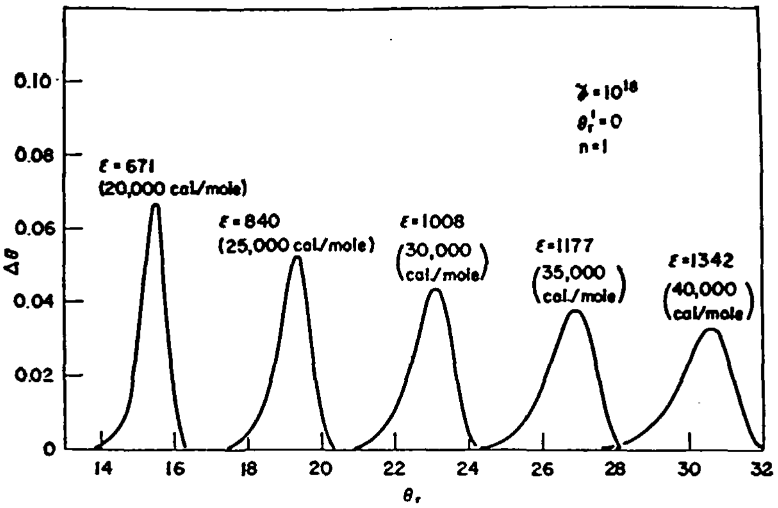


FIGURE 19. Variation of calculated peak shape and temperature with activation energy. (Reed et al.)

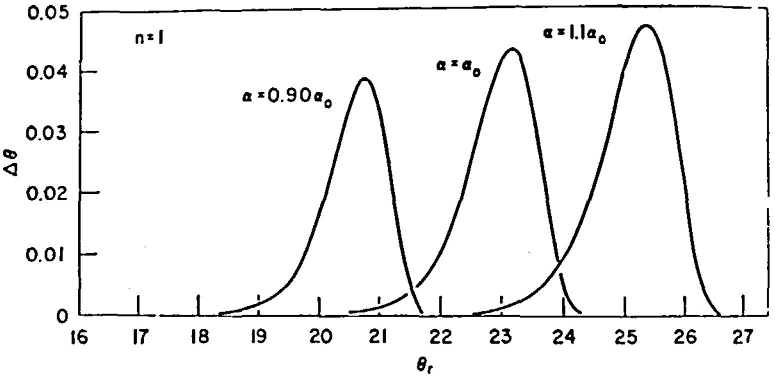


FIGURE 20. Variation of calculated peak shape and temperature with the ratio (*a*) of the heat capacity to the thermal conductivity. (Reed et al.)

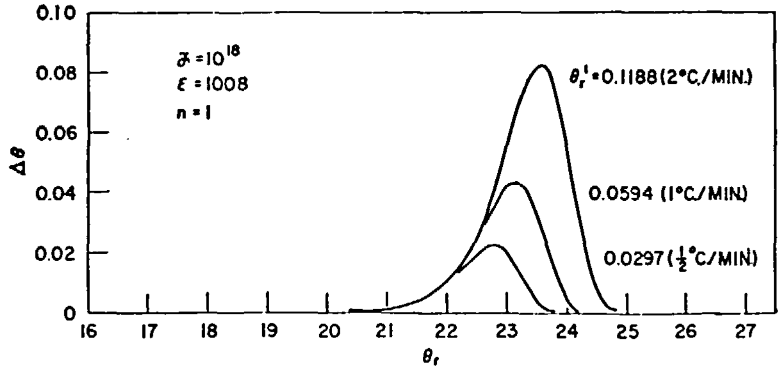


FIGURE 21. Variation of calculated peak shape and temperature with heating rate. (Reed et al.)

apparent increase in peak temperature when less time is taken to reach that peak temperature. But an equally important reason is that the peak temperature is not being measured anyway. Not only is the abscissa a linear function of time rather than temperature, but also the physical arrangement permits the sample to deviate from the plotted temperature during the reaction (see Figure 22). That is, the plot is of f(ΔT) vs. f(T_r) rather than f(T_s). The actual behavior tends to compensate in fact for a limitation arising from the mathematics.

The apparent dependence of $\Delta\theta$ upon order of reaction shown in Figure 23 is not only a consequence of the mathematics, but also in agreement with many observations. In general, of course, the observed variations are either verified by experiment or at worst are not in opposition to experience.

Noting again that the works of Borchardt and Daniels, and Reed, Weber, and Gottfried were limited in theory and practices to homogeneous solutions, let us examine Barrett's study of decomposition of azobisisobutyronitrile, benzoyl peroxide, and diisopropyl peroxydicarbonate. Using a differential scanning calorimeter, with specimens comprising about 3 mg of sample in about 30 mg of di-*n*-butylphthalate, he calculated the rate of heat absorption and the fraction reacted and from these calculated the instantaneous rate constant, *k*, which he referred to the apparent temperature. The measured temperature was corrected by calibration at 125°C at heating rates of 4 to 32°/min using the solid-solid phase transition of ammonium nitrate; the correction was assumed to be valid over the 77 to 147°C range of the experiments.

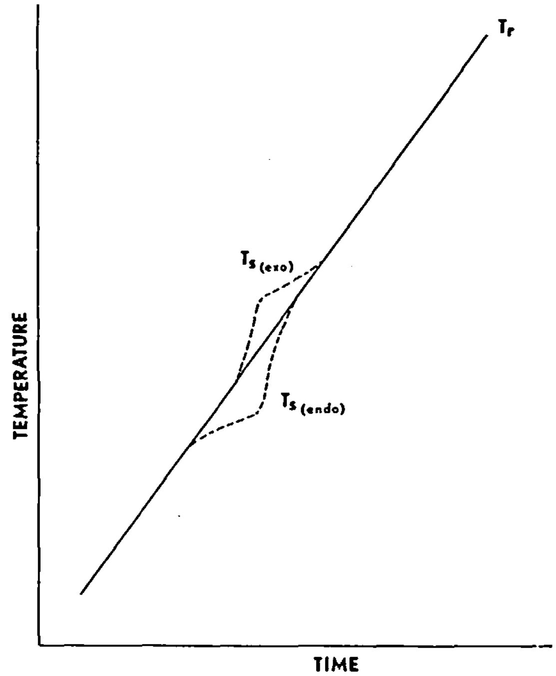


FIGURE 22. Temperature of sample and reference as functions of time at linear heating rates.

The expression for *k* was derived using the curve of Figure 24 and assuming proportionality between the area *a* of a fraction of the peak and the fraction reacted within that time (or temperature) span; between the instantaneous value of the curve dH/dt, and the number of moles then reacting per unit time, he derived an expression for the rate constant, k_t, which simplifies, for these mostly first-order reactions, to

$$k_t = \frac{(dH/dt)}{(A\text{-}a)}, \tag{27}$$

where *A-a* represents the fraction of the unreacted material at temperature *T*.

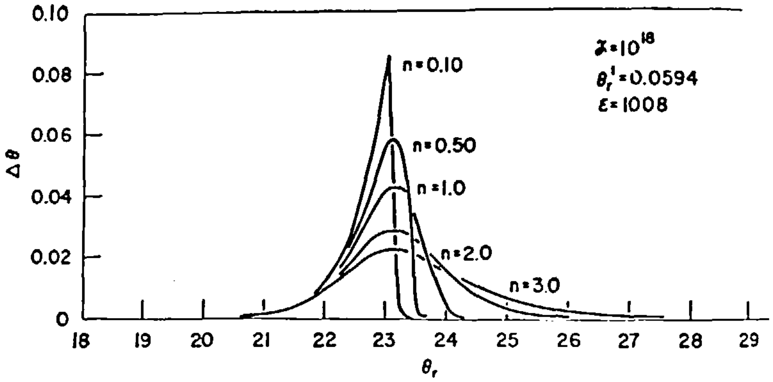


FIGURE 23. Variation of calculated peak shape and temperature with "order of reaction." (Reed et al.)

The results (Figure 25) appear quite straightforward at the fairly high heating rate of 16°/min. The calculated rate constants were correlated with independently obtained (chemical) values at lower temperatures. There is quite good agreement extending to ca. 90% completion.

This agreement shows the major advantage of thermal methods in evaluating the kinetics of reactions in solution: the time span of the experiments can be made small enough that competing reactions are suppressed. For example, the rate constant for decomposition of benzoyl peroxide is about 1.7 x 10^{-2} sec^{-1} at 137°C, while at 70°C it is 1.2 x 10^{-5} sec^{-1}. The reaction at the lower temperatures is complicated by induced decompositions, hence to mixed first and higher order reactions. These higher order decompositions are free-radical reactions and therefore show little

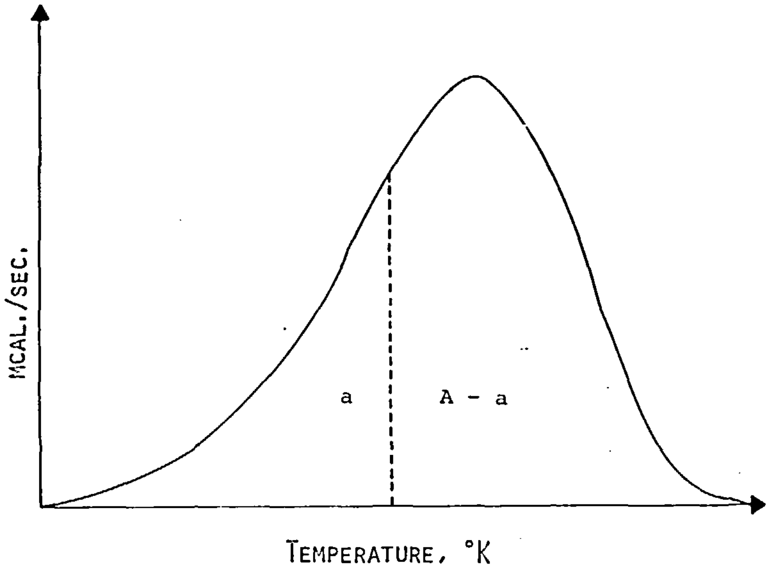


FIGURE 24. Barrett's model peak for kinetic calculations.

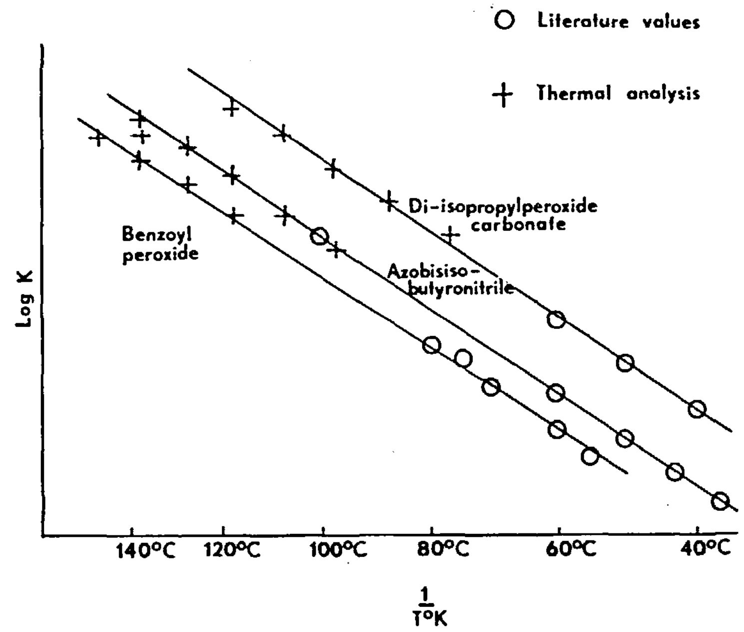


FIGURE 25. Arrhenius plot for the decomposition of polymerization initiators at a constant heating rate (16°C /min.) together with literature values. (Barrett.)

variation with temperature. The primary decomposition rate constant is highly temperature dependent, so the primary reaction can be determined independently by raising the temperature sufficiently so that the material is used up within minutes after a measurable amount of free radical is formed.

Note carefully that this is still valid only for homogeneous reactions, and, equally important, for cases in which a good measure of the heat input is obtained. This latter condition limits the method to calorimetry, differential calorimetry (including DTA with isolated sample and reference holders), and differential scanning calorimetry.

Note that the temperature is being measured elsewhere than at the sample and that the data show quite good reproducibility, so a fairly uniform error in temperature will have little effect on the calculated values.

VARIATIONS IN MATERIALS

The condition of the starting material is highly variable not only in particle size, shape, or surface perfection, but also in total energy. The defects of structure rising from cracks, strains, and other bulk imperfections cause effective perturbation of the rates of reaction already. Distortions due to grinding, radiation, or other treatments can change the behavior of the sample more drastically. But very serious energy differences can exist and persist when material is changed from one chemical form to another. The destruction of a crystalline hydrate chemically does not always lead to immediate collapse of the structure, even though the removal of material allows a rearrangement. Thermodynamic favorability notwithstanding, the remaining chemical entity can retain the old lattice indefinitely in time, and sometimes through substantial increases in temperature. If the material does collapse into its new form, the energy must be released as heat; many exotherms in DTA arising from this event have been reported. The exotherm occasionally noted in calcium carbonate after loss of carbon dioxide is one example. Wilburn, Hesford, and Flower observed it, but concluded that the basis was the sample holder, since their electrical analog treatment of the DTA peak called for an apparent exotherm for a particular sample holder configuration. If their explanation was correct, heat would have to be accorded the qualities of mass, since it would, in this case, display the attribute of momentum.

Speros, Hickok, and Cooper have studied the amorphous calcium monohydrogen phosphate obtained by heating the dihydrate because of the irreproducibility of thermal behavior of similar preparations. Because the $CaHPO_4$ is used in large-scale production of lamp phosphors by subsequent thermal treatment, closely reproducible intermediate preparations are imperative. These authors, observing the irreproducibility, prepared intimate mixtures of hydroxy-apatite and/or octacalcium phosphate with amorphous calcium hydrogen phosphate and obtained curves which varied considerably in form and magnitude as the ratio of calcium to phosphate was changed from 1.0 to 1.1 (Figure 26). The effect virtually disappeared at 1.28. The product of the reaction is $Ca_2P_2O_7$, nearly always the *gamma* form, although some *beta* appeared in some runs.

From the variation of thermal effect by their "quantitative DTA" [earlier described by Speros and Woodhouse (1963)] and from x-ray evidence, they postulated an enthalpy level diagram (Figure 27) which included an amorphous state substantially higher in energy than $CaHPO_4$. They used this set of enthalpy levels to predict the variation in curves by postulating models of combinations as shown in Figure 28. The expected TG as well as the dH/dt curve is shown for each model. They concluded that Model D gave the best description, but that additional study of the nucleation of the $P_3 \rightarrow P_1$ transition was warranted. Furthermore, Models A and B also occur, but no evidence for the rearrangement of the amorphous $CaHPO_4$ prior to reaction was found, even though the energy difference is not less than 2.4 kcal/mol. This is at least one third of the enthalpy change for the $R_1 \rightarrow P_1$ reaction.

The important features pertinent to the present discussion are that:

1. The amorphous reactant *in this case* shows no evidence of rearrangement but undergoes reaction directly. The amorphous state being higher in energy it should react at a higher rate, although the energy difference is small in comparison to the calculated activation energy of more than 70 kcal/mol.
2. An apparently straightforward reaction (on paper) may be complicated in practice by the possibility of alternate paths and uncertainty of the rate-limiting reaction. In the present case, the

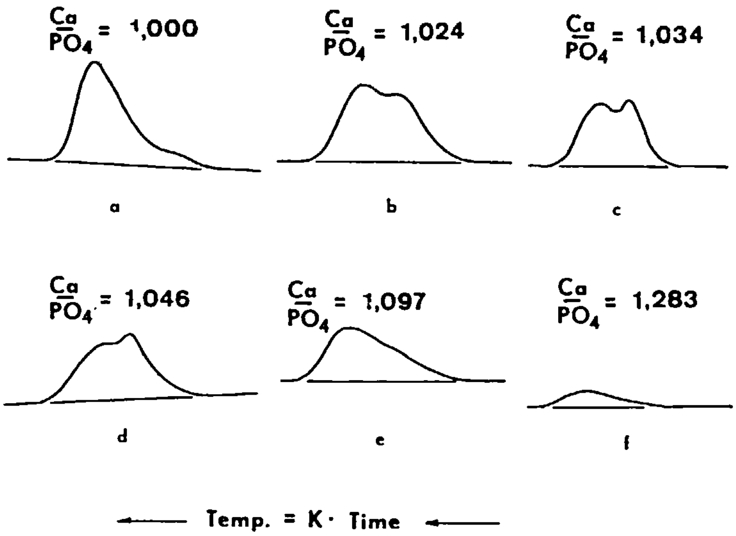


FIGURE 26. Quantitative Differential Analysis records for the thermal decomposition of "$CaHPO_4$" of the Ca/PO_4 values shown. (Speros et al., Proceedings 6th International Symposium on Reactivity of Solids, 1968.)

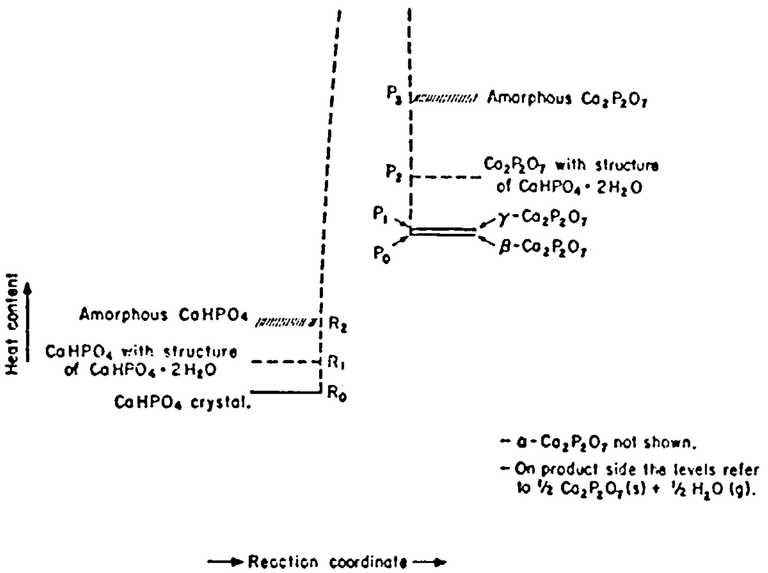


FIGURE 27. "Enthalpy level diagram" for the known possible reactants and products. (Speros et al.)

overall reaction is in part two parallel reactions and in part two successive reactions.

NONHOMOGENEOUS DECOMPOSITIONS

Weber and Roy took note of the change in kinetics of dehydroxylation of clay minerals with water vapor pressure and attempted measurements by differential thermal analysis. Using a capsule with an external thermocouple and enclosed in a much larger sealed vessel, they computed the activation energy and the order of reaction from the area, time, temperature, and differential temperature at a series of points along the DTA peak. They fitted the data to the simple order-of-reaction equation, $-dc/dt = kc^n$, using the assumption that if n is known k can be calculated. But

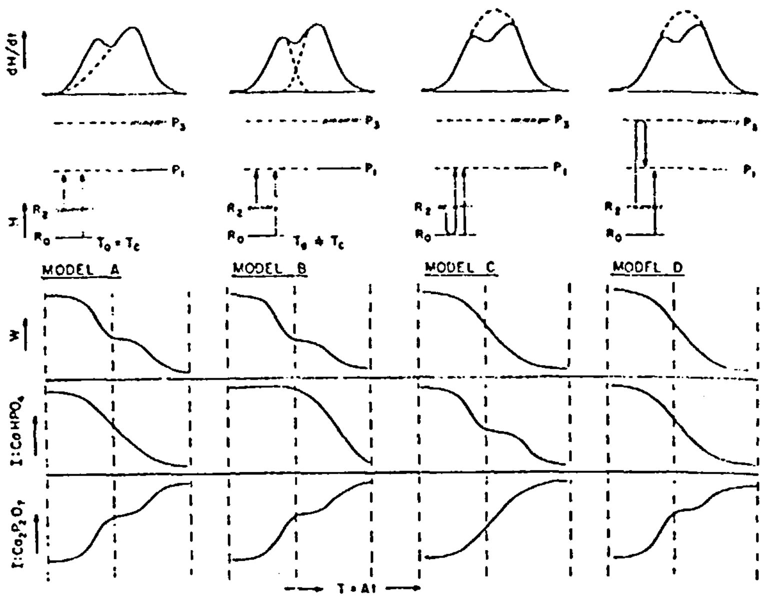


FIGURE 28. First row: Interpretation of the Q.D.T.A. record for the reaction, and corresponding: "enthalpy level diagram" models (second row); expected thermogravimetric behavior (third row) and expected behavior of x-ray diffraction intensity as a function of linearly rising temperature for reactant (fourth row) and product (fifth row). (Speros et al.)

this implies that *c* must be measurable from the DTA curve, so Weber and Roy calculated *dc/dt* from the temperature difference and *c* from the fractional area of the curve, assuming that heat was transferred uniformly to the sample and reference capsules and, of course, no temperature gradient existed within the sample. Neither premise is acceptable without proof.

The transfer of heat from one point to another is directly dependent upon the difference in temperature between the points. At low or high heating rates there is necessarily a difference in temperature between the furnace wall and the sample holders. These isolated capsules will behave independently, so let us assume a steady-state difference of, say, 30°. During the dehydroxylation the sample lags behind the reference due to the heat of reaction. If this lag is, say, 5°, the temperature difference of 35° will permit a 17% greater heat transfer to the sample than to the reference. (If this did not happen, the whole concept of differential thermal analysis would fall to pieces.) This variation in heat supply must take into account not only the heat of reaction but also the heat capacities of the specimen holder. Weber and Roy cite Sewell in justifying the assumption that the total peak area is not dependent upon the specific heat of the sample or its thermal conductivity, but Sewell's computations do not show, at any given point in time during the reaction, that the fraction of material reacted is proportional to the fractional area of the peak up to that time. The assumption is a fair approximation when the specimen is in intimate thermal contact with a heat sink such as a block, but with isolated specimens it is grossly inaccurate. The specimen holder and the sample itself have heat capacities and thermal conductivities which introduce lags in time and hence distortions of the curve.

The assumption of uniform temperature within the specimen is at least equally untenable. The details of construction of the apparatus were not complete but there was no indication that the atmosphere surrounding the capsules was water vapor. Nitrogen or another inert gas can be assumed. The result, of course, is that the material near the open end of this 15 x 2.5 mm cylinder sees a different environment than that at the bottom. The diffusion out of the water vapor and in the nitrogen creates a differing thermodynamic environment along the tube and this in turn leads to differing kinetics, which in turn leads to differing demand for reaction heat and consequently differing temperatures from point to point. The variation in environment is a function of the position, the total pressure, the temperature, the packing, and the rate of evolution of water vapor; not all of these are independent of each other, so computations are impracticable.

Their computation of the "order of reaction" yielded values well scattered between 1.1 and 3.0, with a mean of 2.1 ± 0.8. (The standard deviation is almost as large as the maximum deviation.) The first use of this result is necessary to conclude that the equation chosen is quite untenable. But having selected the "best" value of *n*, Weber and Roy calculated the rate "constant" and from the variation in this parameter with temperature they found an activation energy. Their values (Table 1) vary from 93 to 152 at atmospheric pressure.

In an attempt to explain their values in relation to those of Allison, Murray, and White, or Holt et al., for example, Weber and Roy extended their work to higher pressures (ca. 9 atm) and obtained numerical activation energies (Figure 29) which had a poorly defined relationship to pressure. This is a necessary consequence of forcing the data to fit an equation. The assumptions that (1) the kinetics could be described by a single rate constant and (2) the activation energy does not vary with temperature are particularly unrealistic in the case of kaolinite.

TABLE 1

Kinetic Data for Some Kaolinites [from Weber and Roy] Calculated from $-\frac{dc}{dt} = kc^n$

Source	n	E
Rio Grande, Sao Paulo, Brazil	2.7	111 kcal/mol
Fettlitz, Germany	3.0	147
Cape Province, South Africa	1.3	106
Pugu, Tanganyika	1.3	102
Heystrek, South Africa	3.0	152
Bath, South Carolina	1.1	93
Mesa Alta, New Mexico	3.0	134
Lewistown, Montana	1.9	107
Spruce Pine, North Carolina	1.9	100

A major reason for the deficiencies is the apparent acceptance of the activation energy as the independent variable. As Ingraham pointed out, the activation energy is often determined procedurally as the temperature coefficient of the rate of reaction. To ascribe any more meaning than that would require a precise knowledge of the mechanism, that is, the activated species and the manner in which it attained from either reactants or products. Even to find a realistic value would require firm knowledge of the equation followed. And to acquire this firm knowledge would require better definition of the experimental conditions. Assuming an inert gas was used, the water vapor pressure at the bottom of Weber and Roy's capsule, once the reaction is well begun, is almost certainly equal to the applied pressure and the material there will react slowest and finish last. The material at the top may experience a total pressure of 9 atm, but at a water vapor pressure of 0 atm at the beginning of the experiment, this would increase to some value dependent upon the amount of water released, the total volume of the furnace chamber, and possibly the temperature of the coldest part of the chamber. But with constant

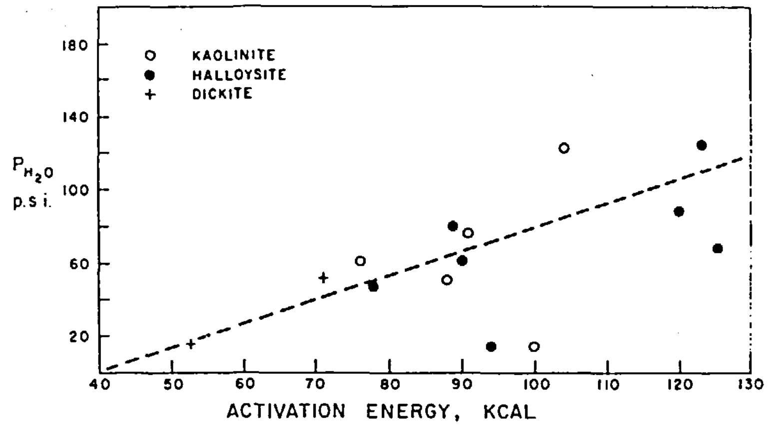


FIGURE 29. Pressure dependence of the activation energy for dehydration of kaolinite, dickite, and halloysite at water pressures between 20 and 130 psi. (Weber and Roy.)

specimen size, the water vapor pressure in the furnace chamber will reach some limiting value which is unrelated to the total pressure in the system and which is the same for all experiments at all pressures. Furthermore, because the diffusion of gases is time dependent, variation with heating rate can be expected.

The variation in calculated activation energies suggests that there are very real differences in energies of the reacting systems. Nevertheless, the fact that various observers do find common values indicates some real basis other than diligence in searching the literature. To the extent that the activation energy is a "temperature coefficient" of the rate of reaction and $k = F(\alpha, T, P_1, P_2, \cdots, P_n)$ is the basic equation, a partial explanation can be offered.

Supposing the actual rate constant to be describable in terms of the temperature, the pressure(s) of the gas(es) produced, and the fraction of material remaining, the several contributions would appear in some fixed manner.

Qualitatively, these may be separable so that the relationship

$$k = f_1(\alpha)\, f_2(T)\, f_3(P) \tag{28}$$

may be set down, and even if $f_3(P)$ should really be $f_3(P,T)$ there is no substantial error. That is, the contribution of I is small in comparison to that of *P*. It would appear, then, that if *k* were measured either at some fixed α in separate experiments, or if the value of α did not change greatly within the experiment, *OR* if $f(\alpha) = 1$ (that is, zero order), the physical measurement of $d\alpha/dt$ at different temperatures will reflect $\partial k/\partial T$ with little perturbation. The introduction of a tenfold error in *k* would simply cause a unit displacement of a plot of *d log k* vs. 1/T without changing the slope. Allowing now for minor deviations from the assumptions, good agreement between investigators could still be expected, provided reasonable and similar experimental conditions are used.

Even with substantial changes in experimental conditions, errors in the activation energy would arise only when the other "independent" variables had, themselves, a substantial dependence on temperature or, of course, if the reaction was proceeding rapidly enough that the need to supply the enthalpy increment changed the temperature distribution.

The methods of differential calculus are extremely useful when properly applied. The "properly applied" must refer to the system being described as well as the mathematics describing it. The major fault lies in differentiating an expression with respect to a single variable without making sure that all other variables are held constant physically as well as mathematically. An important source of error here is an incomplete expression for the dependent variable. If k_T is differentiated with respect to *T* and the result is treated as a total derivative, it will be in error in every case in which a reversible step uses or supplies a gaseous material. The failure to include a pressure term is the source of the error and leads to calculations of activation energies which may vary by an order of magnitude. The slowing of a reaction as the equilibrium pressure is approached leads to an increase in the calculated activation energy if the ordinary version of the Arrhenius equation is used without taking account of the reverse reaction.

The dehydroxylation of kaolinite was also studied by Toussaint, Fripiat, and Gastuche by vacuum thermogravimetry. They were largely concerned with separating the intraparticulate processes from the diffusion process within the powder mass. The latter can be controlled rather easily by imposition of a known pressure of water vapor on the system, but Toussaint et al. accepted the proposition that the diffusion within the particle cannot be separated from nucleation and growth. On the other hand, they accepted the need for an order-of-reaction description, suggesting that the velocity of reaction was related to the concentrations of solid and vapor by

$$V = kC_s^{n_s} C_v^{n_v}, \tag{29}$$

where n_s and n_v are the orders with respect to the solid and vapor products of the reaction.

Attempting to determine n_s and n_v, they prepared 0.4 g cylinders of kaolinite (10.6 mm high and 7.4 mm dia.) by drying a paste. (They verified that powder in a crucible behaved similarly.) They heated the sample isothermally in a thermobalance, measuring the temperature in an already calcined cylinder beneath the sample. In some experiments, they stopped the runs at average fractional dehydroxylations of 0.30 and 0.70 and found that water contents of concentric cylinders cut from the sample varied with radius. The outer cylinder, of course, lost the most water

(Figure 30). The gradient in water content is greatest for the higher temperatures (485 to 490°). The lower gradient at the lower temperatures (430 to 435°) led them to restrict the larger part of their work to the lower temperatures, studying the variation of decomposition rate with varying external pressures of water vapor as in Figure 31, or at constant pressure over a range of lower temperatures. From a set of data at 4.3 mm, plotted as *log* (100 − *a*) vs. time in Figure 32, they deduced that the decomposition was first order with respect to the solid phase, so long as the reaction had not reached 70% completion. The probability that any reaction can be induced to follow first-order kinetics at low enough rates is discussed elsewhere.

The conclusions reached by Toussaint et al. are of prime interest. From these and other data, they conclude that the reaction proceeds by successive dehydroxylation of complete octahedral layers, but that the reaction probability is proportional to the amount of unreacted material (first order). This would imply that a layer in the center of a particle is as likely to react as one adjacent to already reacted material. They cite "second moment" calculations from nuclear magnetic resonance in support, deducing from the small change in the second moment that no significant change in the average OH-OH distance has taken place up to 70% reaction. But this argument does not limit the possibility to a layer-by-layer sequence. It shows, in effect, that where hydroxyls are close enough to interact the change is not great. This argues against purely first-order random dehydroxylation, but certainly not against a randomly located nucleation and growth mechanism (Figure 33). When the nuclei are very small, their contribution is insignificant and when they have reached a diameter of many OH-OH distances, they also have little effect on the computed value, although the intensity would diminish. At some intermediate time, when the

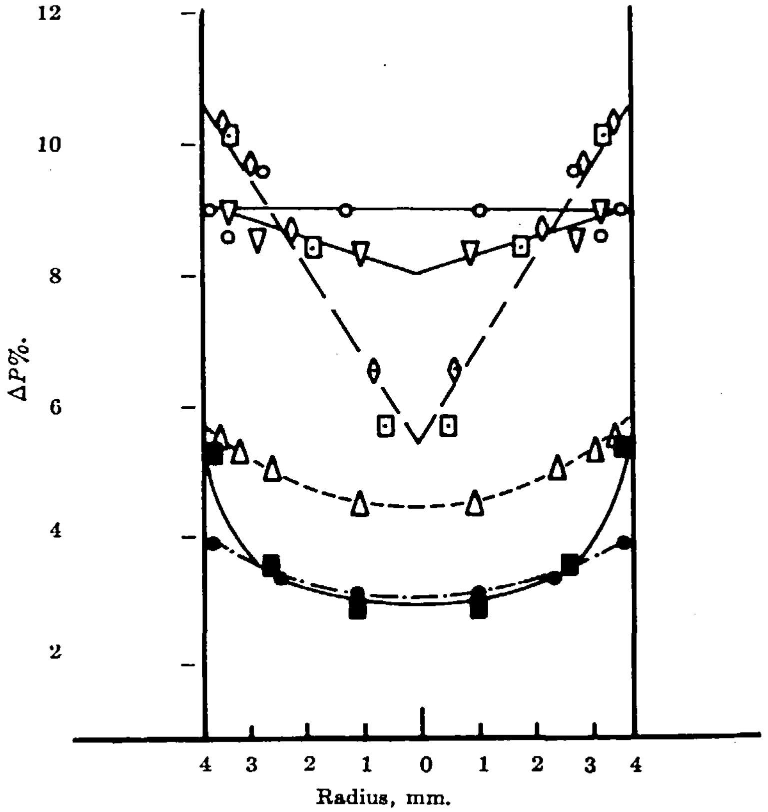


FIGURE 30. Gross diffusion process. Water loss (ΔP%) as a function as the radius in mm. Upper curves, $\alpha \simeq 70$: ◇, 490°, $P_{H_2O} = 12.9$ mm; ⊡, 490°, $P_{H_2O} =$ 1 mm; ○, 431°, $P_{H_2O} = 0.6$ mm; ▽, 430°, $P_{H_2O} = 11$ mm. Lower curves $\alpha \simeq$ 30: △, 435°, $P_{H_2O} = 11.3$ mm; ○, 430°, $P_{H_2O} = 11.6$ mm; ⊡, 485°, $P_{H_2O} = 0.7$ mm. (Toussaint, Fripiat, and Gastuche.)

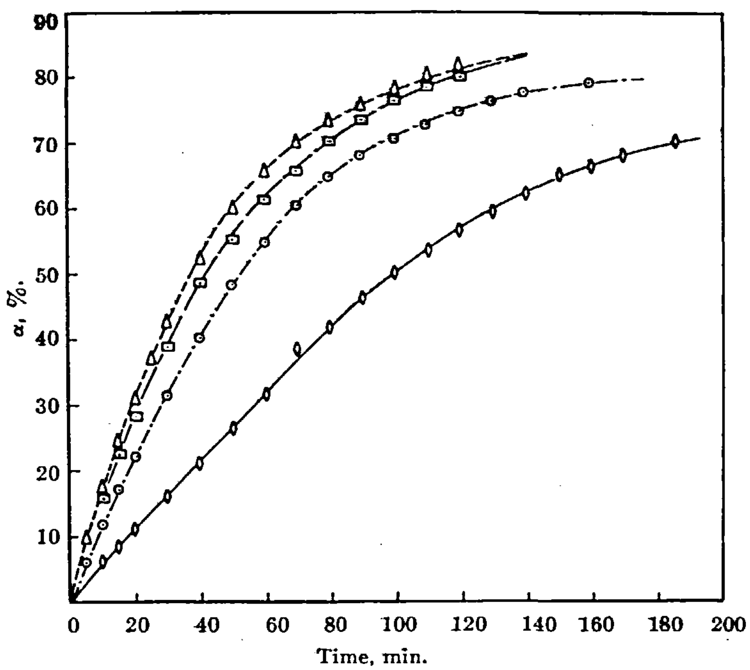


FIGURE 31. Dehydroxylation process at constant temperature (431°) under different pressures: P_{H_2O} = 0.8 mm, △; 0.9 mm, ⊡; 4.3 mm, ○; 11.2 mm, ◇. (Toussaint, Fripiat, and Gastuche.)

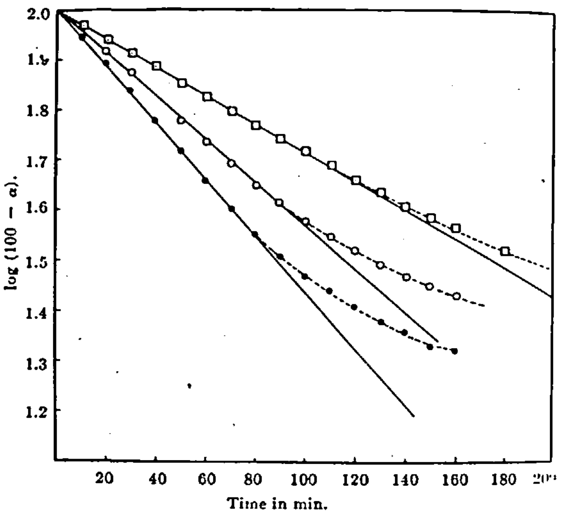


FIGURE 32. First-order rate law with respect to the solid phase: P_{H_2O} = 4.3 mm, ⊡ at 408°; ○ at 422°; ○ at 431°. (Toussaint, Fripiat, and Gastuche.)

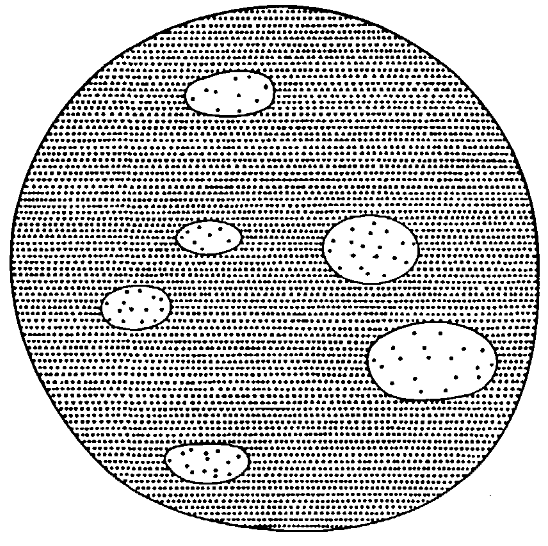


FIGURE 33. Partially decomposed kaolinite assuming nucleation and growth model and possible isolating of -OH groups.

nuclei are large enough to affect the signal but small enough that the technique can "see across" it or "see" the occasional -OH left behind and isolated, there might be a diminution in the second moment, indicating an increased average distance. Their data show a value of 4.6 at $a = 0.0, 0.32, 0.40$, and 0.51, but 4.4 at $a = 0.15$ and 4.3 at $a = 0.67$. It is not known if this transitory 4% decrease is significant. Similarly, the decrease at $a = 0.67$ may be due to the increasing significance of the isolated hydroxyls not so much because of their total number as because of the diminutions of the major contribution due to the well-ordered material.

Toussaint et al. calculate n_V as ca. 0.2 for a pressure of 4.3 mm, noting that it increases with the pressure regardless of the extent of dehydroxylation. They ascribe this behavior to an adsorbed water film, noting a similarity of their rate data to the Langmuir isotherm. Very low occupancy of adsorption sites on the dehydroxylated layers would be anticipated because of the temperature, but a process of adsorption, residence, desorption, diffusion, adsorption, residence, etc. would decrease the overall diffusion rate. The pressure would decrease the rate by decreasing the mean free path and hence increasing the collisions with the surface. The ascription would appear to be plausible.

But none of the conclusions take account of the reversible step evident from the data of Fripiat and Toussaint, who were able to substitute deuterium for 50% of the constitution hydrogens, as well as from various other reports. The inhibition of diffusion may possibly be the primary mechanism of limitation, but this is by no means clear from the data given. Indeed the proton delocalizations suggested by Fripiat and Toussaint support a reversibility which is at variance with the description of a simple dehydroxylation.

Brindley and Nakahira have concluded that if the effect of water vapor can be eliminated the dehydroxylation is indeed first order. They measured the rates of decomposition of a number of discs of kaolinite of various thicknesses, plotted log w/w_0 vs. t (Figure 34), extrapolated the values for various thicknesses to zero thickness (infinitely thin disc), and found a straight-line relationship which corresponds, of course, to a first-order reaction. (The w/w_0 is the fraction of total weight loss.) The times taken to reach a given fractional weight loss, w/w_0, vary in quite good agreement with a linear relationship $tw/w_0 = c + kh$, where h is the thickness and hence c is the time at zero thickness; the agreement appears to be good not only in the initial (straight-line) portion but also in the curved part of the plot.

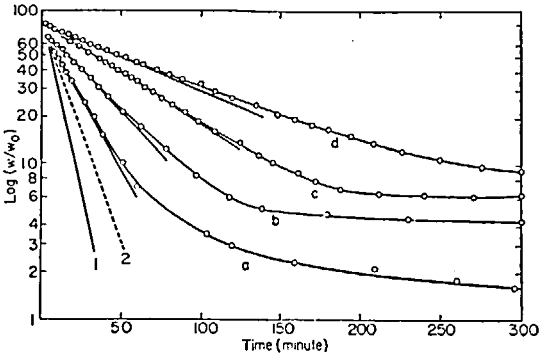


FIGURE 34. Variation of log (w/w_0) with time for kaolinite disks heated at 497°C; (w/w_0) is expressed as a percentage of the total weight loss by dehydroxylation. Curves a, b, c, and d correspond to disks of thickness 0.38, 0.83, 1.55, and 2.68 mm, respectively. Curve 1 is the extrapolated curve for an infinitely thin disk and curve 2 corresponds to a very thin layer of uncompacted powder. (Brindley and Nakahira.) The weight loss is decidedly dependent on the geometry of the specimen.

Brindley and Nakahira use the rate constants determined from the initial portions of the curve to establish the inherent behavior of kaolinite; they were able to show (Figure 35) that the rate constant at each of several temperatures varied linearly with thickness. They established further that an Arrhenius plot is linear *only* for infinitely thin discs (Figure 36). The same general behavior was demonstrated by *halloysite*, another *kandite*.

On the other hand, Murray and White measured the rate of weight loss of kaolin under constant (furnace) temperature and concluded that the dehydroxylation in the 500 to 600°C range is a first-order reaction. They eliminated the extra-crystalline water by heating to constant weight at 430°C; then they raised the furnace temperature rapidly to the desired temperature and observed the weight loss as a function of time. They plotted their data with the appropriate coordinates and concluded that over the bulk of the decomposition range the decomposition followed a first-order law.

They assumed uniformity in temperature both with respect to position and with respect to time. Both are unlikely. Hills (1967) has shown that the center of a sphere of calcium carbonate drops in temperature by as much as 40°C at a temperature

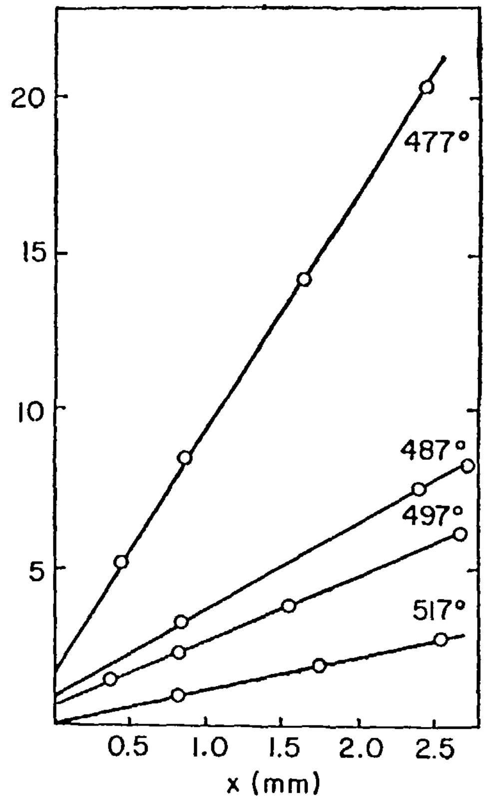


FIGURE 35. Variation of reciprocal rate constant, $1/k$, vs. disk thickness for kaolinite disks at various temperatures. (Brindley and Nakahira.) The distance through which vapor must diffuse has a very clear effect on the rate.

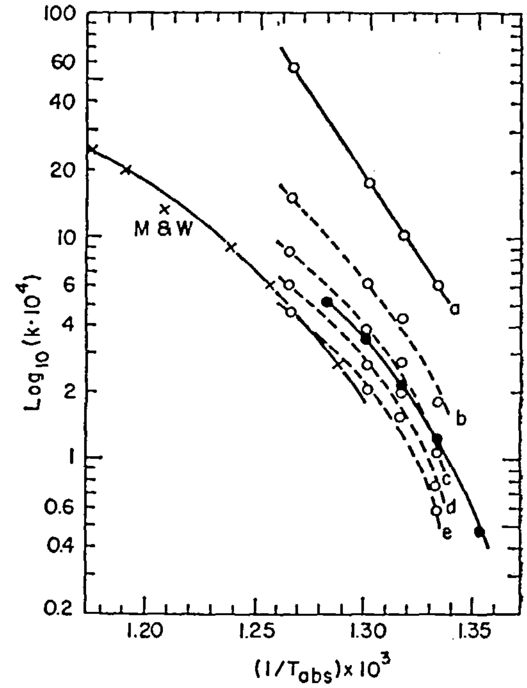


FIGURE · 36. Arrhenius plots for log k vs. $1/T$ for kaolinite. Curves a through e correspond to disks of thickness 0, 0.5, 1.0, 1.5, and 2.0 mm, respectively. Curve M & W shows data by Murray and White. Solid circles show experimental data for sample held in a small platinum crucible. The Arrhenius plot is linear only for curve a corresponding to the infinitely thin disk. (Brindley and Nakahira.) In an infinitely thin specimen the decomposition should follow a first-order law.

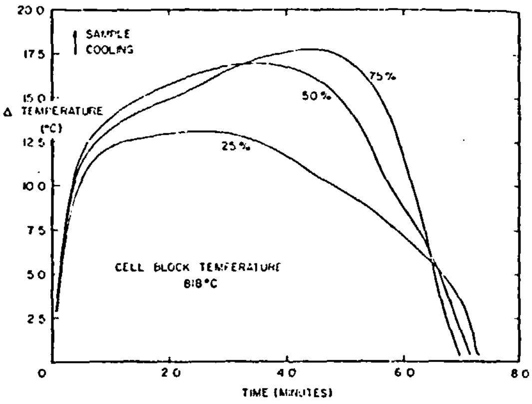


FIGURE 37. Sample cooling during reaction, as indicated by thermocouples placed 25, 50, and 75% of the distance from the bottom to the top surface of the $CaCO_3$ sample. (Ingraham and Marier, from Schwenker and Garn.)

at which the decomposition was proceeding slowly enough that the whole reaction required more than an hour. In a much shorter time period, 6 min, Ingraham and Marier (1968) found deviations of 20°, and variations within the cell block from top to bottom as shown in Figure 37. The deviations for kaolinite ought to follow a different pattern from those of calcium carbonate, but the general behavior should be somewhat similar for the same reaction times. Without debating now the rate control of the calcium carbonate decompositions, the total heat supply required per mole is about the same, ca. 40 kcal; for kaolinite, $\Delta H \approx$ 160 cal/g compared to ca. 400 cal/g for calcium carbonate.

Murray and White found it necessary to determine graphically an $l\infty$ and express the first-order rate equation as

$$\log\left(\frac{l_\infty - l}{l_\infty}\right) = -kt \qquad (30)$$

where $l\infty$ is the total loss of weight and l the loss at time, t. This was necessary because the dehydroxylation does not proceed to completion at all temperatures. Brindley and Nakahira have found similar results; the decomposition proceeded to some limit which was dependent upon the temperature. Murray and White's l^{∞} is large enough relative to the total quantity of water to warrant prediction of a noticeable gradient. Considering the other evidence on rates and on atmosphere effects, it is apparent that mass and heat transport introduce some phase boundary behavior and that the dehydroxylation of kaolinite is not a first-order reaction, nor does it follow first-order kinetics very well. Sewell has also pointed out that Murray and White's description cannot be regarded as more than a first approximation.

The work by Brindley and Nakahira does not really eliminate the effect of water vapor. The extrapolation to zero thickness is an extension from 1.0 and 0.5 mm; the latter is about 2 x 10^5 times the mean free path, so the extrapolation cannot be accepted as definitive. Note too that Holt, Cutler, and Wadsworth found the parabolic rate law to be applicable, concluding that the rate of reactions was governed by diffusion within the particle.

Hills reports that several characteristics of a chemically controlled reaction can also be shown by a process controlled by heat and mass transfer. The constant reaction rate per unit area of reaction front which is characteristic of a phase boundary decomposition can be simulated by a mass transport process. Noting that if a chemical step limits the reaction, the initial rate of reaction will be substantially less than that calculated for mass transport control; he suggests this as a test for chemical vs. mass transport control.

Hills also shows that if thermal diffusion is taken into account instead of gaseous diffusion, the shape of the reaction curve can still resemble that of a phase boundary chemically controlled reaction. The heat must get not only to the specimen but also through the product layer to the reacting material. Hills shows (Figure 38) the importance of measuring the sample temperature

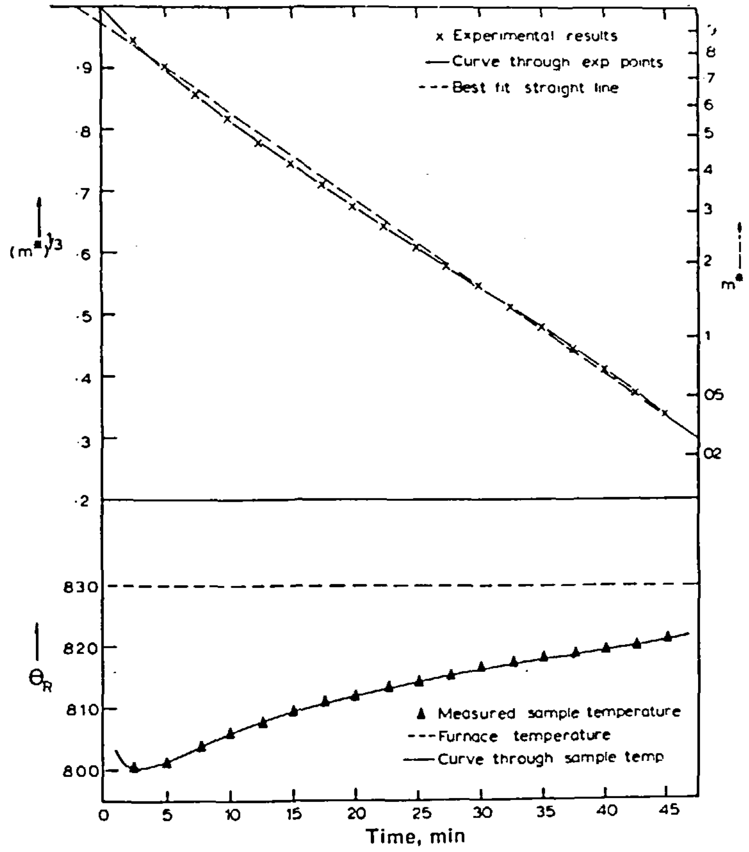


FIGURE 38. Experimental plot of $(m^*)^{1/3}$, and sample temperature against time, for calcium carbonate sample decomposing in pure air in a furnace held at 830°C. (A. W. D. Hills.)

directly rather than assuming its temperature from measurement of the environment. The decrease in temperature due to taking up of heat is enough to slow the initial reaction. Forty thousand calories per gram mole is not a small amount; removal of one thousandth of it will lower the temperature by 1.5°. Rapid reaction of 1% of a sample of calcium carbonate will lower the temperature 15°, more than enough to affect the rate of reaction substantially. Hills concludes that the calcium carbonate decomposition is controlled by heat *and* mass transfer, and that chemical control is unimportant. The error in temperature measurement can be especially severe in thermogravimetry where a nearby thermocouple is often the source of temperature data. Newkirk showed the severity of the error (Figure 39) during the several reactions of calcium oxalate monohydrate.

The physical realities of structure on the atomic-molecular level cannot be ignored. An assembly of atoms and/or ions do not obey only the laws or relationships we happen to be studying. They still obey the law of gravity, equilibrium relationships where applicable, diffusion laws, and the requirements imposed by chemical bonding. The last is as often overlooked as the others.

Whether a material will react or not depends upon many parameters besides the free energy difference between reactants and products. One of the requirements is that the reactants can meet. The access of a fluid reactant to a solid reactant is often limited by a solid product. The limitation may range from a moderation of the flow through severe inhibition of diffusion to complete blockage of flow. Dismissing liquid-solid systems from consideration here, the process bringing about the limitation may be chemical, mechanical, or both.

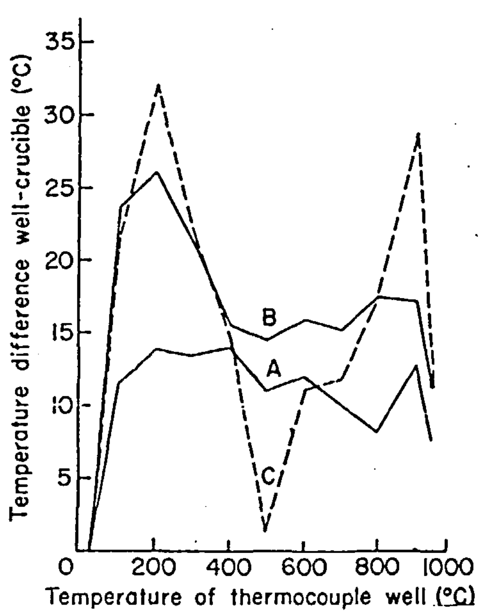
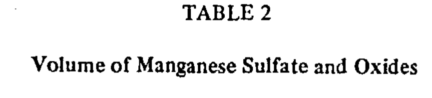


FIGURE 39. Temperature lag due to sample. Decomposition of $CaC_2O_4 \cdot H_2O$. Heating rate 600°C/hr: A, crucible only; B, crucible + 0.2 g $CaC_2O_4 \cdot H_2O$; C, crucible + 0.6 g $CaC_2O_4 \cdot H_2O$. (Newkirk, from Garn, 1965b.) The temperature lag varies the most at the temperatures of greatest interest.

An example of mechanical stoppage can be taken from the works of Ingraham and Marier in which they were studying the formation and decomposition of $MnSO_4$ from and to the oxides of manganese and sulfur dioxide. They formed pellets of the oxides at ca. 7,000 atm, the pellets having a mass of ca. 1 g and an area on each face of ca. 1.6 cm². Attempting to determine the kinetics of the formation of the sulfate by heating the pellets in 2:1 mixtures of SO_2 and O_2, they found it possible to obtain "initial reaction rates" from the data of Figures 40 and 41, but could not follow the reaction beyond ca. 10% because it stopped. The formation of $MnSO_4$ in the surface layers essentially seals off the remaining oxide because the specific volume of $MnSO_4$ is substantially greater than that of any of the oxides. This is reasonable because the formation reaction involves insertion of an S-O linkage into the Mn-O-Mn bond. That is,



Calculating the volumes per mole of manganese reveals that the volume increase is by a factor of 2 to 3.

TABLE 2

Volume of Manganese Sulfate and Oxides

Material	Volume of compound containing 1 mole of Mn
MnO_2	17.3 cm³
Mn_2O_3	17.8
Mn_3O_4	15.7
$MnSO_4$	46.4

The manganese sulfate fills the paths by which the sulfur dioxide could migrate into the pellet. The stoppage is not immediate because several

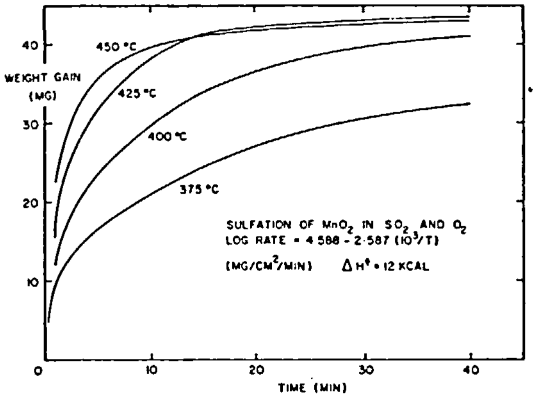


FIGURE 40. Rate data for the sulfation of MnO_2 in 2:1 mixtures of SO_2 and O_2. (Ingraham and Marier, 1968.)

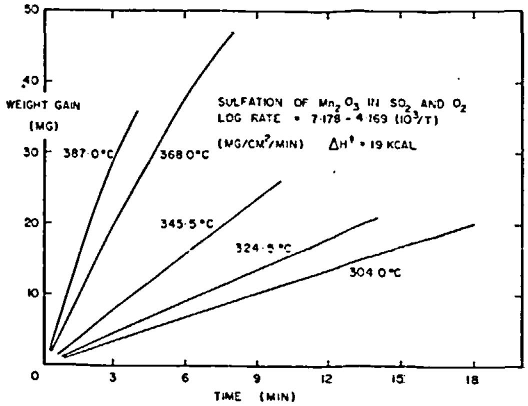


FIGURE 41. Rate data for the sulfation of Mn_2O_3 in 2:1 mixtures of SO_2 and O_2. (Ingraham and Marier, 1968.)

layers along the passage would have to react, and diffusion to the unexposed layers is already inhibited somewhat by reaction of the first layers. Initial reaction rates can be measured, but the significance of any but the very early measurements is diminished considerably.

This is also an example of the interplay of several factors in the observed reaction rate during a real experiment. The manganese oxides were pressed firmly enough to cohere, even on heating. Now consider the formation of the sulfate at the surface and in the ubiquitous pores. The new compound forms to greater and greater extents until, with some inevitable mismatching, the advancing material from opposing walls meets. The completed material, the reaction product, is necessarily displaced from the reaction site because of the extended bonds. The one-by-one addition of SO_2, presumably not with simultaneous addition of oxygen, will also lead to a poorly formed lattice because of uneven distribution of the gaseous reactants. The total effect of the poor lattice coupled with the easier deformation of the extended Mn–Mn bond renders the manganese sulfate unable to break the structure in which it is embedded and equally unable to break loose from it. If a large isolated particle was heated under the same conditions, the sulfate layer could be expected to flake off from the parent particle because the volume change is so great and more or less isotropic. The kinetics could be expected to follow an advancing-reaction-front law, with occasional discontinuities as flaking occurs. An assembly of uncompacted particles ought to show similar behavior without the discontinuities. This is by no means a certainty. There are a few cases of self-limiting reactions in lightly compacted materials, possible because of similar behavior within the particle. The additional effects due to the mechanical forces in chemical reaction would be a very worthwhile field of study.

While the sealing-off process is common to the oxides, there are still quite noticeable differences between the behaviors of MnO_2 and Mn_2O_3 or Mn_3O_4, the latter two being rather similar. The MnO_2 reacts more slowly and has a calculated activation energy substantially smaller than the others, 12 kcal compared to 19 and 21 kcal. This difference presumably represents true differences in the chemical process.

But looking at the practical problem of reacting sulfur dioxide with manganese oxide, whether the primary object is entrapment of the sulfur or formation of manganese sulfate, the reaction would not be carried out in this manner. The relevance of data to conditions quite unlike those under which they were collected is discussed in another section.

Ingraham and Marier found that the oxidation of Mn_3O_4 to Mn_2O_3 and Mn_2O_3 to MnO_2 behaved quite differently. As might be expected, the decomposition steps also behave differently. The decomposition curves of MnO_2 to Mn_2O_3 tend to follow a sigmoid shape (Figure 42), while the $Mn_2O_3 \rightarrow Mn_3O_4$ curve (Figure 43) follows a more typical pattern. Here a volume effect may also be involved. The intermediate state has a larger volume than either of the others, so the

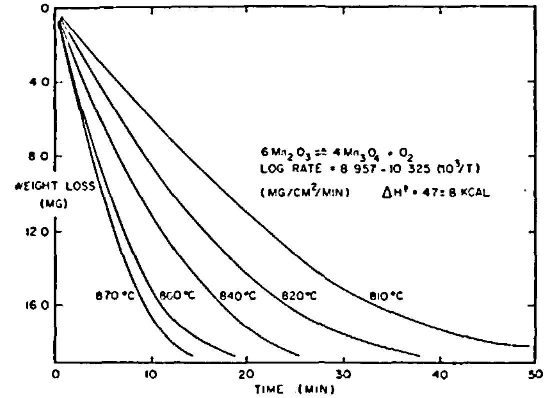


FIGURE 42. Rate data for the decomposition of Mn_2O_3 in a stream of nitrogen. (Ingraham and Marier, 1968.)

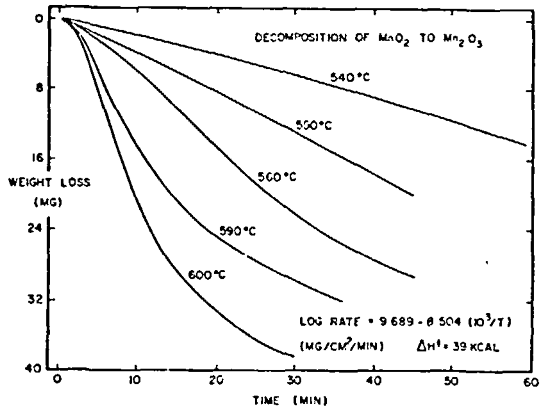


FIGURE 43. Rate data for the decomposition of MnO_2 to Mn_2O_3 in a stream of nitrogen. (Ingraham and Marier, 1968.)

tendency to fill the cavities and inhibit further decomposition is very real. There is an important difference between the decomposition and the formation; the pressure differential in formation is limited to the imposed pressure while the pressure inside a particle has no such limit. The decomposition may well be retarded, but not stopped, by the closing of the pores in the compacted sample.

CALCIUM CARBONATE – A REVERSIBLE DECOMPOSITION

The numerous studies on calcium carbonate have provided a substantial background of knowledge. The material has a fairly high heat of decomposition, in the vicinity of 40 kcal, depending on the temperature at which the decomposition is carried out. It is also reputed (1) to decompose at a rate dependent only upon the supply of heat (provided the carbon dioxide pressure does not exceed the equilibrium vapor pressure) and (2) to decompose at rates describable by a chemical rate constant.

Ingraham and Marier accept the chemical rate constant concept and have devised another method to measure the rate and activation energy. They use, in effect, the transient cooling of the sample (in an otherwise isothermal system) during the decomposition reaction. The reaction must be impeded in some way until the isothermal condition is reached; Ingraham and Marier applied an atmosphere of carbon dioxide to the system until it had reached a steady state. They initiated the reaction by switching a 45 cm^3 min^{-1} flow of argon into the system. The carbon dioxide pressure immediately dropped to a value below the equilibrium vapor pressure, so the calcium carbonate began to decompose. Because the argon swept *through* the sample, each particle was surrounded by an argon atmosphere containing more or less carbon dioxide.

The result was a more or less homogeneous reaction within the sample holder. A marked cooling (Figure 37) took place as the heat of reaction was supplied first by the particle, then from the block. The need for the large heat-of-reaction prevented immediate complete decomposition of the particles at the bottom (in contact with pure argon), and hence prevented the rise of the carbon dioxide pressure to a high value. Because the carbon dioxide pressure did not become high, the decomposition could proceed throughout the sample. The time required for completion of the reaction was used in describing the kinetics of the decomposition.

Ingraham and Marier established the near-homogeneity of reaction by placing thermocouples (presumably along the axis) at various depths in the sample holder. This has a fairly predictable result: the temperatures along the axis, being most distant from the source of heat, all drop substantially and more or less uniformly. One may also predict that thermocouples distributed along a radius would show a gradient because of the need to transport heat to the center. The bottom thermocouple temperature tends to be higher because of the end effect; the heat is transported not only from the side but also from the bottom of the well. Also, the gas is preheated.

The experiment could be improved by omitting the flow of *any* gas after the equilibration. Quick lowering of the pressure to some known pressure below the equilibrium vapor pressure would initiate the reaction without the distracting presence of a diluent. Stone had devised a somewhat similar method to detect and measure moisture. He lowered the pressure on the sample until the moisture evaporated. The heat effect gave a fair quantitative measure of the moisture.

Speros and Woodhouse (1968) studied both the decomposition and recomposition of calcium carbonate, finding an enthalpy change of ca. 42.4 kcal/mol, an activation energy of 44.0, and an empirical reaction order of 0.20. They heated the sample in dry nitrogen for decomposition and a mixture of carbon dioxide and nitrogen (ca. 0.02 atm CO_2) for recombination. They fitted (Figure 44) the recombination to the equation $dH/dt = B/H^y$ finding values of y in the 0.15 to 0.38 range for temperatures between 42.0 and 480°C. The reaction became diffusion limited as it progressed and virtually ceased before completion. Successive decomposition recombinations led to lower and lower values, indicating in part the sintering-annealing of the CaO particles and in part the blocking of the CO_2 by the already formed $CaCO_3$ during recombination. This latter effect was also observed by the present author in unpublished work on calcareous ocean sediments.

Ingraham and Marier calculated an activation energy of 47 kcal/mol for reagent grade calcium carbonate. Muraishi reported 99.7 and 60.6 for calcium carbonate and calcite, respectively.

Using a flow of helium mixed with another gas, Wist examined the effect of this other gas on the decomposition of calcium carbonate. Predictably, carbon dioxide and carbon monoxide repressed the reaction, but when a high enough temperature was reached, the apparent temperature dependence was very slight. The calculated activation energy was, of course, quite high, in agreement with other authors. Adding a CO_2 pressure term brought the apparent activation energy down to 40 kcal/mol.

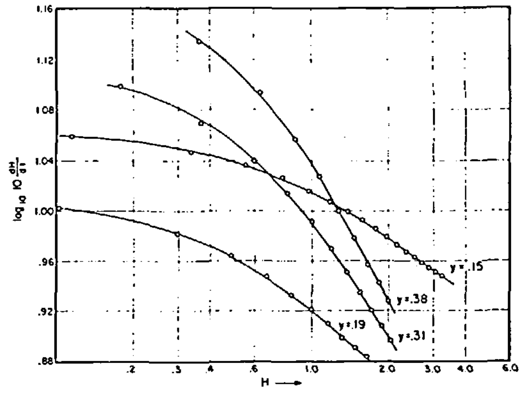


FIGURE 44. Plots of data from QDTA records utilizing the equation $dH/dt = B/H^y$. (Speros and Woodhouse.)

Nevertheless, the presence of oxygen or hydrogen as well as carbon dioxide or carbon monoxide affected the measured rate of decomposition and apparent activation energy even though the sample was a pellet, rather than a batch of easily accessible (to the atmosphere) fine powders. The reasons for the variations are not completely clear, although some speculations are offered by Wist. Variations in the thermal conductivity of the gas will have an effect which was not taken into account. A pellet at 1,000°K will still be heated partly by conduction. It is highly probable that the temperature distribution varies from gas to gas, and the actual temperature of the reaction interface is neither the measured temperature nor reproducibly different from the measured temperature in different gases. We may note that hydrogen is reported (by Wist) to have a "catalytic effect on the reaction rate" compared to pure helium. Hydrogen is a superior conductor of heat, and the only one.

Assuming that the equations

$$\frac{d\alpha}{dT} = k\, f(\alpha) \text{ and} \tag{31}$$

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{32}$$

are descriptive of the reaction, and a constant heating rate so that

$$T = T. + \beta t, \tag{33}$$

Sharp and Wentworth eliminate k and derive the logarithmic form

$$\ln\left(\frac{1}{f(\alpha)} \cdot \frac{d\alpha}{dT}\right) = \ln\frac{A}{\beta} - \frac{E}{RT}. \tag{34}$$

Plotting the left-hand side against 1/T, they determine E and A from the slope and intercept of the "straight-line." With assumed "orders of reaction" of 1/2 and 2/3, corresponding to movement of an interface through a disk and sphere, respectively, they found for calcium carbonate activation energies of 43-8 and 45-8 kcal/mol, respectively.

Their comparison with other methods was described earlier.

The implicit assumption of a single reaction mechanism is probably valid in the case of calcium carbonate. The assumption that the temperature of the sample is describable by Equation 33, however, is quite untenable. We can reasonably assume that the sample is following the programmed temperature quite well, up to the beginning of the decomposition (Figure 22). In order to carry out the decomposition, 440 cal are needed for their 1-g sample, although less than 0.3 cal were needed for each degree previously. That is, at their heating rate of 255°/hr they were supplying about 1.2 cal/min to the sample; temperature gradients between furnace and sample holder and through the sample holder and sample were established to maintain this supply.

Then, somewhere near 600° there is a call for ca. 1,500 times this amount of heat before the reaction can be carried out and the heating proceed under the extant CO_2 pressure. (The calcium carbonate decomposition is well known to be reversible.) Obviously the temperature differential must change to supply *any* more heat, so the rise in temperature virtually ceases. Instead, a little decomposition occurs as the temperature differential increases. The increase in carbon dioxide in the atmosphere allows the remaining carbonate to warm further, but still slowly, as the temperature increases still further. Instead of a rate controlled reaction there is a continually varying rate which tends to increase because of the increasing temperature differential, but the increase is inhibited by the increasing partial pressure of carbon dioxide. This accounts for the completion ca. 900° of a reversible reaction which began ca. 600°. The major delay is due to the need to establish a temperature differential large enough to supply heat rapidly.

Note that phase transitions require far less heat, yet the temperature of the sample ceases to rise (Figure 45), or greatly slows its rise, during the event (Garn, 1968). Note, too, that in agreement with other observers, Sharp and Wentworth's "activation energy" is actually the enthalpy change for the reaction.

APPARATUS EFFECTS

Some errors in kinetic analysis are inherent in the method of measurement. The fact that the thermocouple (or other transducer) measures only its own temperature is noted elsewhere. The effect of the placement of the thermocouple outside the sample is to obscure the meaning of an instantaneous measured value; that is, the measured value depends upon the amount of heat reaching the thermocouple, whether or not the sample is receiving a proportional amount of heat *and* rising in temperature in the same manner as the thermocouple. Figure 46 shows simplified views of some of the possible configurations relating the heat source, the sample, and the thermocouple. The typical block with axial thermocouple will show the best response specifically to the behavior of the sample. It will require a large enough sample to provide a complete shield against direct influence of the block temperature upon the thermocouple temperature. That is, all the heat must traverse the sample. This becomes impracticable for quite small samples.

The interposition of the measuring device between the sample and heat source provides a good measure of the energy traversing the transducer, but how well the temperature is related to the measured temperature depends upon the resistance (to heat flow) of the intervening material (see Figure 47). Assuming a zero-order process, Brennan, Miller, and Whitwell have calculated some of the effects of varying the thermal resistance R and found that the calculated rate of melting of polyethylene is substantially affected by changes in R. For example, if the contact area between the sample pan and the sample was changing, there would be an apparent change in the rate of melting. They conclude that the kinetic analysis of the data would be affected by the sample size and even shape because of changes in contact area. Other types of sample holders with thermocouples outside the sample show different relationships between the heat path and the sensing element. Two types of sample cups are compared with a block with axial thermocouple in Figure 48. The irregular traverse of the holder by the heat is not amenable to calculation even in steady-state heating. During a high demand the pattern would be distorted still more. Since the small cups give greater sensitivity, they are very useful for DTA. Calculations of kinetic parameters, though, are exceedingly unrealistic.

On the other hand, the cups would yield a better calorimetric measurement than the block.

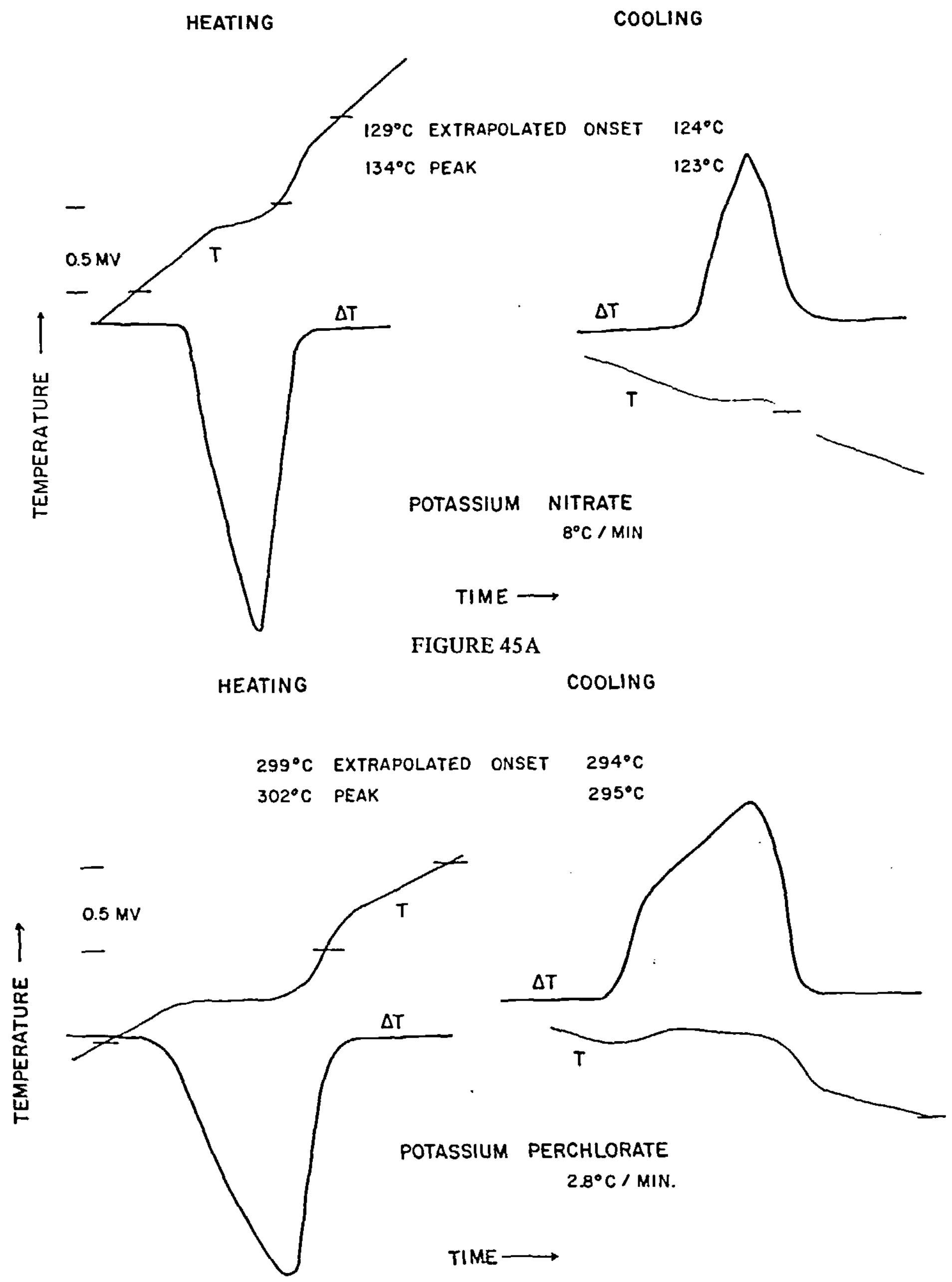


FIGURE 45A

FIGURE 45B

FIGURE 45. DTA curves for (a) potassium nitrate and (b) potassium perchlorate showing variation of the temperature in the sample as a result of consumption of heat due to the change of state.

REEXAMINATION OF THE ACTIVATION ENERGY

Even though different observers may independently determine kinetic parameters using different models, for a given decomposition there is a degree of consistency for some reactions which might seem astonishing to the nonkineticist. Even this infrequent consistency calls for some more detailed examination of the activation energy and the specific rate constant.

Note first that, as pointed out earlier, the calculated activation energy includes the enthalpy change for the reaction, which is generally the

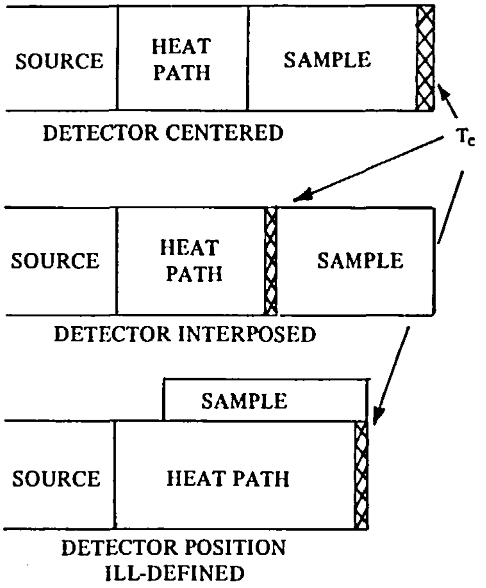


FIGURE 46. Representation of heat paths and points of measurement for a centered thermocouple (or other detector), a detector interposed between the heat source and the sample, and a detector not in either position. (Garn, 1971.)

largest component. The reality of thermodynamics, then, specifies a lower limit to the calculated value. The variations in extra energy to reach the activated state are relatively small perturbations, so broad agreement is almost inevitable. Still, there is substantially more than chance agreement for many reactions, yet wide variation for others.

The variation in calculated activation energies suggests that there are very real differences in energies of the reacting systems. Nevertheless, the fact that various observers do find common values indicates some real basis other than diligence in searching the literature. To the extent that the activation energy is a "temperature coefficient" of the rate of reaction and $K = f(\alpha, T, P_1, \cdots, P_n)$ is the basic equation, a partial explanation can be offered.

Supposing the actual rate constant for a single reaction process to be describable in terms of the temperature, the pressure(s) of the gas(es) produced, and the fraction of material remaining, the several contributions would appear in some fixed manner.

Qualitatively, these may be separable so that the relationship $K = f_1(\alpha)\, f_2(T)\, f_3(P)$ may be set down. Even if $f_3(P)$ should really be $f_3(P,T)$ there is no substantial error. That is, the contribution of T is small in comparison to that of *P*. It would appear, then, that if *K* was measured either at some fixed *α* in separate experiments, or if the value of *α* did not change greatly within the experiment, *or* if $f(\alpha) = 1$ (that is, zero order), the physical measurement of $d\alpha/dt$ at different

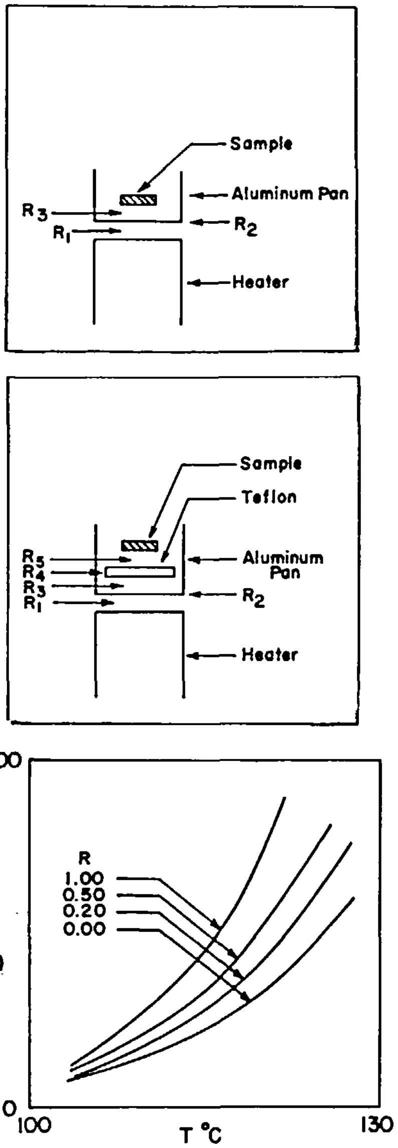


FIGURE 47. Resistance to heat transfer; (a) normal operating arrangement showing interfacial resistances R_1 and R_3 and pan transfer resistance R_2; (b) with Teflon disc added showing additional interface R_5 and transfer resistance R_4 through Teflon disc, adjustable by changing the disc; and (c) the effect on the rate of melting of polyethylene due to the added transfer resistance (in this case external to the sample). (Brennan et al.)

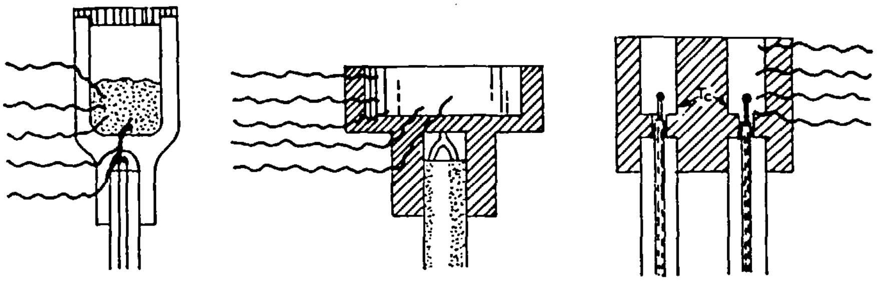


FIGURE 48. Simplified representation of heat paths for sample holders with centered and noncentered thermocouples. (Garn, 1971.)

temperatures will reflect $\partial k/\partial T$ with little perturbation. The introduction of a tenfold error in k would simply cause a unit displacement of a plot of $d \log k$ vs $1/T$ without changing the slope. Allowing for minor deviations from the assumptions, good agreement between investigators could still be expected, provided reasonable and similar experimental conditions are used.

Even with substantial changes in experimental conditions, errors in the activation energy would arise only when the other "independent" variables had, themselves, a substantial dependence on temperature or, of course, if the reaction was proceeding rapidly enough that the need to supply the enthalpy increment changed the temperature distribution.

The methods of differential calculus are extremely useful when properly applied. The "properly applied" must refer to the system being described as well as the mathematics describing it. The major fault lies in differentiating an expression with respect to a single variable without making sure that all other variables are held constant physically as well as mathematically. An important source of error here is an incomplete expression for the dependent variable. If k_T is differentiated with respect to T and the result is treated as a total derivative, it will be in error in every case in which a reversible step uses or supplies a gaseous material. The failure to include a pressure term is the source of the error and leads to calculations of activation energies which may vary by an order of magnitude. The slowing of a reaction as the equilibrium pressure is approached leads to an increase in the calculated activation energy if the ordinary version of the Arrhenius equation is used without taking account of the reverse reaction.

THE PRAGMATIC APPROACH

From the scientific viewpoint, rates of reaction and activation energies are possible keys to determination of reaction mechanisms. Hence, detection of changes in rates, implying changes in mechanisms, is highly important. The deviation from an easily described behavior probably indicates a unique characteristic that may lead to better knowledge of the material or class of materials.

There are other very practical reasons for knowing rates of reaction and their temperature dependences. Design of processing equipment and selection of processing conditions impel industry to obtain measures of these parameters because increments of temperature or time represent added operating expense. The manufacturer will attempt to balance costs of time, costs of fuel, and costs of capital equipment to obtain the lowest cost per unit at the planned level of production. For this purpose, an overall rate of reaction measured under empirically predetermined operating conditions may be the starting point; variations are then introduced singly or in combination to ascertain their effects on the overall rate.

Even though this latter use may generally gloss over the "fine structure" of a rate *vs.* time (or temperature) plot in favor of treating large masses as simply as possible, more detailed knowledge is still of potential value for new or unusual materials.

In many cases authors have described purely empirical evaluations of k and E. Furthermore, several models other than those described herein have been developed for solid-state decompositions, generally for very special cases. Šesták and Berggren have examined a number of these models and noted that a few terms are common to virtually all of them. From this study, they have suggested that an improved analytical form could be obtained by use of three terms in $f(\alpha)^x$. Their equation,

$$\frac{d\alpha}{dt} = k\,(1 - \alpha)^n\,\alpha^m\,(-\ln(1 - \alpha))^p,$$

would provide a closer fit to real data than any single expression describing a particular model.

Mathematically, this is an obvious consequence. The more terms used, t, the more accurate the description, just as a fine brush can give a better representation than a palette knife, while the palette knife enables a greater production of pictures. But instead of looking at the equation as a means of fitting the data more closely, we can look at it as a tool to learn more about the nature of the decomposition. The equation takes into account most of the several possible influences operating to determine the overall kinetics of the process. It must be recognized that in this form the exponents must be treated first in a very pragmatic way, as purely mathematical terms. From the relative magnitudes of the exponents (derived from experimental data) some conclusions might be obtainable. If a reaction is accurately describable by a more limited expression, for example, using two of the terms, the third exponent will go to zero. Hence, for any reaction, if any exponents approach zero closely, mechanisms requiring that term may be dropped from consideration. Very little more can be learned from the equation.

With the present methods of data acquisition and treatment, it is possible to obtain "best values" of *n, m,* and *p,* although with considerable initial effort in developing the program. Once the program is developed, however, the evaluations of the exponents for another reaction, or for the same reaction under different conditions (atmosphere or pressure, for example), are not difficult, while interpretation still is. The computed values will reflect the influence of concurrent processes and hence have some indistinct meaning because several models invoke two of the exponential terms.

The temptation to find the best values of the exponents for one reaction, then another, and another is undoubtedly strong, but this would overlook the real capability of the computer and data acquisition equipment. The evaluation of the three exponents and *k* in principle could be determined from four values of $d\alpha/dt$ or five consecutive values of α (with equal Δt's) and additional values simply improve the precision. Accumulation of several hundred data points during a single run is not difficult. Computation of the several constants for the whole set of data should be performed as a matter of course. If *all* the data fit the equation well, the values are ready for interpretation. In the more probable case, the values will not fit well throughout the course of the reaction, so the next step in computation can be taken.

The typical computer can be programmed to perform the computations over a continuously changing set of data. One may take, arbitrarily, a set of 20 consecutive measurements and compute the *best values* of the constants, then move along the data set in increments of 1 or more (depending upon the budget) adding in the next group of values and dropping the earliest. The multiple computations of *k, m, n,* and *p* would disclose trends in values which may in turn be relatable to a changing mechanism.

For nonisothermal experiments, the Arrhenius equation can be used, if desired, in the initial computations or the values of $k(\tau)$ used in separate computations to evaluate the apparent activation energy. The number of data points being computed should be adjusted so that the temperature change over the set is small; the smaller the better, within the range of practicality.

It is fairly safe to predict that most solid decompositions will show variations in the exponents due to changes in the physical process. Young has shown that as many as five discernible regions may be found in a plot of α vs. t (isothermal), and Hulbert's results have already been mentioned.

A changing process should become evident from changing values of the three exponents, but the *overall* rate constant may change in an unpredictable manner. If the immediate goal is evaluation of the apparent activation energy, some smoothing may be necessary. If the need to refine the interpretation of the data is great enough, the single rate constant describing the overall process might then be replaced by separate rate constants, k_m, k_n, and k_p, in a new set of computations to ascertain the relative contributions and estimate an activation energy for each process.

A relatively large number of data points obtained under carefully controlled conditions (and checked for reproducibility) could be used with confidence in deducing the nature of decomposition processes at various stages of the whole decomposition. The technology is available. The ability to delineate the several processes should be a tremendous aid in understanding the nature of particular decompositions.

The computation process can be used with other equations, or with Sěsták and Berggren's with an added term or two.

SUMMARY

Thermoanalytical techniques offer attractive ways of determining kinetic parameters. There are obvious convenience and economy in making a single set of measurements in a few hours and performing extensive computations while the equipment is generating data on another material. This apparent gain in efficiency has led to considerable effort in planning computations which lead to easy extraction of the activation energy, the apparent kinetic order, and the rate constant from a single curve. To enable these computations, simplifying assumptions had to be made. The following statements provide a set of cautions based on past work.

Nearly all solid decompositions are topochemical in nature. Many reactions have some reversible step which leads to effects due to changing atmospheres or pressures.

The variation of k with τ does not provide an accurate measure of the activation energy except under very reproducible conditions. The derivative $d\ln k/d(1/\tau)$ is a partial, not a full, derivative and there is generally no certainty that the other variables are held constant.

The energy states in a solid material do not vary statistically because there is no way to establish an equilibrium distribution. Both the total energy and distribution of energy states are influenced greatly by the history of the sample.

The added energy of the surface *plus* its immediate contact with the atmosphere *plus* its higher temperature during heating will cause it to react differently from the bulk. This also introduces a particle size effect.

Decompositions do not necessarily proceed by a single mechanism; hence, different rate constants and activation energies would apply to different stages. These stages are not necessarily separated.

Pressure effects are not easily isolated because gases need to diffuse through particles to reach or leave the reaction site.

Reaction products and hence subsequent reactivity are affected by the atmosphere.

Direct measurement of the sample temperature is vital for kinetic treatments. The self-cooling during any but very slow reactions can cause the temperature to deviate greatly from the programmed temperature.

The general form of the DTA peak can be simulated by calculations based on homogeneous kinetics. The variability of real peaks indicates that other models are actually operative.

Thermodynamic heats of reaction are in many cases the only limit on reaction rate. The activation energy has this enthalpy change as its lower limit.

Heat transport and mass transport or a combination of them can simulate a chemical control on reaction velocity.

Mechanical effects due to expanding or contracting crystal structure may limit the agreement with any single model.

Modern methods of data acquisition make it possible for the experimenter to accumulate enough data from a single experiment to permit greatly extended data treatments. Enough data can be acquired and stored to offer hope of separation of contributing mechanisms.

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Research Council for Figure 10; *American Mineralogist* for Figures 15 and 29; John Wiley & Sons for Figures 26, 27, and 28 from *Reactivity of Solids* and Figures 24 and 25 from the *Journal of Applied Polymer Science*; National Research Council of Canada for Figures 11 and 12 from the *Canadian Journal of Chemistry*; and Mettler Instruments for Figures 3 and 5.

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