

KINETICS IN SOLIDS

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ABSTRACT

The kinetics of solid state reactions generally cannot be assumed to follow simple rate laws that are applicable to gas-phase reactions. Nevertheless, a widely practiced method for extracting Arrhenius parameters from thermal analysis experiments involves force fitting of experimental data to simple reaction-order kinetic models. This method can produce significant errors in predicted rates outside the experimental range of temperatures, and it is of limited utility for drawing mechanistic conclusions about reactions. In this review, we discuss how an alternative "model-free" approach to kinetic analysis, which is based on the isoconversional method, can overcome some of these limitations.

INTRODUCTION

Chemical kinetics is the study of reaction rates. Although there are many reasons for quantifying the rate of a chemical reaction, two stand out as being particularly important. The first is that by parameterizing the reaction rate as a function of state variables such as temperature, pressure, and concentration, the rate of reaction can be predicted for any set of conditions, regardless of whether the rate has actually been measured under those conditions. The accuracy of the prediction depends on the functional form used for the parameterization and how close the set of conditions is to those used for determining the parameters. The second major reason for carrying out kinetic studies is to investigate reaction mechanisms. One of the fundamental tenets of chemical kinetics is that no reaction mechanism can ever be proved on the basis of kinetic data alone; at best, one may demonstrate that a proposed mechanism is consistent with the kinetic data. Furthermore, kinetic analysis may not be the most efficient means

of determining a reaction mechanism (1); however, it is extremely useful for drawing reasonable mechanistic conclusions (2, 3).

For practical purposes, all solid state reactions must be activated by external stimuli. Thermal activation and photoactivation are by far the most common methods, but other means such as application of pressure, magnetic field, and electrochemical potential are also possible. Barrierless reactions (e.g. self-reactions of free radicals) can be studied in gases and liquids where mixing is possible, but reaction in the solid state can be studied only for cases in which the reactants are in a metastable state. In this review, we focus our attention on methods of kinetic analysis for thermally activated reactions, especially those taking place above room temperature. For a discussion of experimental studies of solid state reactions taking place at cryogenic temperatures, the reader is referred to a recent review (4).

Solid state kinetic data are of practical interest for the large and growing number of technologically important processes. Several of these processes have been the subject of recent reviews, including, for example, thermal decomposition of crystalline solids (5) and energetic materials (6), thermal oxidation and decomposition of polymers (7) and coals (8), crystallization of glasses (9) and polymers (10), and solidification of metallic alloys (11). The most up to date information on a wide variety of materials studied by thermal analysis techniques can be found in a comprehensive review by Dollimore (12).

The most common experimental techniques employed to study kinetics of thermally activated reactions are thermogravimetry (TG), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). These techniques are widely applicable to many types of reactions but are not chemically specific in their means of detection. The TG technique, for example, measures mass loss from a sample due to gas formation as a function of time and/or temperature during a specified heating program. The overall reaction rate determined by TG corresponds to the rate of gas formation, which may or may not be the process of interest. Fortunately, many solid state reactions involve at least partial conversion of the sample to the gas phase, and TG is therefore widely used. DSC measures the power required to keep the sample and a reference material at the same temperature throughout a specified temperature program. Similarly, DTA measures the temperature difference between the sample and a reference material when both are subjected to the same heat flux. These techniques are universally applicable to kinetic analysis because all reactions involve changes in enthalpy. However, the techniques by themselves do not provide any information about the nature of the reaction. For this reason, thermal analysis techniques are sometimes combined with chemically specific detection methods such as Fourier transform infrared (FTIR) spectroscopy, mass spectrometry (MS), and gas chromatography (GC) to analyze

gaseous products. X-ray diffractometry (XRD) as well as FTIR and electron paramagnetic resonance (EPR) spectroscopy are also used as complementary techniques to analyze solid reaction products. Whereas TG, DSC, and DTA can provide important measures of the overall (global) kinetics of thermally stimulated reactions, the aforementioned complementary techniques permit a deeper insight into the mechanism of solid state reactions. The data obtained by the chemically specific techniques are sometimes subjected to kinetic analysis, the results of which are helpful in elucidating the overall kinetic scheme (13–17).

The kinetics of thermally stimulated reactions are normally studied under the conditions of isothermal and/or nonisothermal (usually linear) heating. A major problem of the isothermal experiment is that a sample requires some time to reach the experimental temperature. During this period of nonisothermal heating, the sample undergoes some transformations that are likely to affect the results of the following kinetic analysis. The situation is especially aggravated by the fact that under isothermal conditions, a typical solid state process has its maximum reaction rate at the beginning of the transformation. This especially restricts the use of high temperatures. Nonisothermal heating (e.g. following a linear temperature program) resolves these problems and has therefore become more popular in the field of solid state kinetics than the classic isothermal experiment. However, the advantages of the nonisothermal experimental technique are at least partially offset by serious computational difficulties associated with the kinetic analysis. In this review, we consider some of the important issues associated with kinetic analysis of nonisothermal kinetic data. The ultimate goal is to find the best means of treating kinetic data in order to provide reliable methods of reaction rate parameterization (i.e. those with meaningful predictive value) and the means for gaining a better understanding of the physical and chemical characteristics of solids that affect chemical reaction rates.

BASIC PROBLEMS OF NONISOTHERMAL KINETICS

The concepts of solid state kinetics (18–20) came into being from a wealth of isothermal experiments well before the first instruments for nonisothermal measurements became commercially available. The established formalism of isothermal kinetics has been extended to nonisothermal conditions. If we use the variable α to denote the extent of reaction, then the basic kinetic equation is

$$d\alpha/dt = k(T)f(\alpha), \quad 1.$$

where t represents time, T is the temperature, $k(T)$ is the temperature-dependent rate constant, and $f(\alpha)$ is a function called the reaction model (5, 9), which describes the dependence of the reaction rate on the extent of reaction. In fluid

Table 1 Set of alternate reaction models applied to describe the reaction kinetics in heterogeneous solid state systems^a

Reaction model		$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^2
6	Mampel (first order)	$1 - \alpha$	$-\ln(1 - \alpha)$
7	Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1 - \alpha)^{2/3} (1 - (1 - \alpha)^{1/3})^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Second order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$

^aAdapted from References 5 and 9.

media (gases and liquids) $f(\alpha)$ would describe the dependence of the rate on the concentration of reactants and/or products. However, in solids, where molecular motion is highly restricted and reactions are dependent on local structure and activity, the concept of concentration dependence is much less useful. Furthermore, the extent of reaction depends on the choice of experimental observable (e.g. mass loss, heat transfer, or formation of a specific reaction product). Therefore, the reaction model, $f(\alpha)$, usually plays the role of an empirical function. Several different functional forms of the reaction model are shown in Table 1. Some of them (e.g. first-order, second-order) are suggestive of concentration-dependent reaction models, but due caution must be exercised in making this type of interpretation.

Equation 1 is often used in its integral form, which for isothermal conditions becomes

$$g(\alpha) \equiv \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T)t. \quad 2.$$

For nonisothermal conditions, we can eliminate the explicit time dependence of the kinetic equations by use of the heating rate. In the case of a constant heating rate, $\beta = dT/dt$, we can make the trivial transformation

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt}, \quad 3.$$

in which case Equation 2 takes the form

$$g(\alpha) \equiv \int_0^\alpha [f(\alpha)]^{-1} d\alpha = \frac{1}{\beta} \int_0^T k(T) dT. \quad 4.$$

For most reactions, the Arrhenius equation provides a good description of the temperature dependence of the rate constant. Substitution for $k(T)$ in Equation 4 yields

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT, \quad 5.$$

where E and A are the Arrhenius parameters (activation energy and preexponential factor, respectively). Using this formalism, the global reaction kinetics are completely specified by three pieces of information: the reaction model and the two Arrhenius parameters. This is sometimes called the kinetic triplet. The time required to achieve any particular extent of reaction can be determined for any chosen value of temperature for isothermal conditions by rearranging Equation 2, or for any chosen value of the heating rate, β , by rearranging Equation 5.

The use of the Arrhenius equation in solid state kinetics has been extensively criticized from a physical point of view (21, 22). Garn (22) emphasized that the Arrhenius equation is meaningfully applicable only to those solid state systems that exhibit kinetics of a homogeneous type. The applicability of the Arrhenius equation is believed to be primarily associated with the physical interpretation that we ascribe to experimentally determined values of the activation energy and preexponential factor. If the values of E and A are to be interpreted in the terms of the transition state theory, the Arrhenius equation does not seem to be applicable to solid state reactions. This is not because the theory was developed for gas-phase reactions. The basic concept of a free-energy barrier is fully suitable for solid state kinetics when describing the rates of nucleation and nuclei growth (23) as well as of diffusion (24). All these theoretical considerations lead to equations of an Arrhenius type where E is related to the enthalpy of activation and A to the frequency of lattice vibrations (23, 24). Even if the Maxwell-Boltzmann energy distribution is not applicable to the immobilized constituents of a solid, Galwey & Brown (25) have shown that energy distribution functions of similar form (Fermi-Dirac statistics for electrons and Bose-Einstein statistics for phonons) characterize the most energetic quanta and give rise to an Arrhenius-type equation. Thus, the use of the Arrhenius equation is not only justifiable in terms of a useful empirical parameterization, its use and physical interpretation are supported by a sound theoretical foundation.

On the other hand, an actual obstacle to interpretation of experimentally determined values of E and A lies in the nature of the experiments. The aforementioned standard experimental techniques as well as more sophisticated methods

(26, 27) do not provide complete isolation of an elementary reaction (nucleation, nuclei growth) uncomplicated by diffusion, adsorption, desorption, and other physical processes. In other words, experimental techniques used in solid state kinetics generally do not measure the reaction rates of elementary steps but instead measure the overall rate of a process that usually involves several steps with different activation energies. For this reason, experimentally derived Arrhenius parameters of a solid state process tend to have an overall (effective) nature. By virtue of their effective nature, Arrhenius parameters of solid state reactions are difficult to interpret in the terms of the transition state theory. Therefore, a sound way to settle the issue of the applicability of the Arrhenius equation is to use it and to treat computed Arrhenius parameters as effective constants unless mechanistic conclusions are justified by ancillary data.

McCallum & Tanner (28) have reported that data from nonisothermal experiments can yield inconsistent values of the Arrhenius parameters. As a result, they claimed that use of the Arrhenius equation in the differential rate expression, Equation 1, is inappropriate for nonisothermal conditions. Their argument takes the following tack. First, the extent of reaction α is written as a function of time and temperature,

$$d\alpha = \left(\frac{\partial \alpha}{\partial t} \right)_T dt + \left(\frac{\partial \alpha}{\partial T} \right)_t dT. \quad 6.$$

In a nonisothermal experiment the temperature is a function of time only, so we can rewrite Equation 6 in the rearranged form

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t} \right)_T + \beta \left(\frac{\partial \alpha}{\partial T} \right)_t. \quad 7.$$

This equation implies that the reaction rate (and therefore the kinetic parameters) are dependent on the heating rate in the experiment. That is, the "true" Arrhenius parameters can only be determined by carrying out a series of experiments and extrapolating the results to infinitely slow heating rates (isothermal conditions). The original hypothesis has been effectively refuted by numerous arguments (see Reference 9 and related references therein). One of the most compelling arguments is that α is not a state function, because its value depends on the path taken to a particular combination of T and t . Therefore, Equation 6 cannot be written as an exact differential. Even if Equation 7 is considered valid for a limited set of conditions, the contributions of each of its terms must be considered. The first term represents the kinetic contribution to the reaction rate, whereas the second represents a static or thermodynamic contribution. For solid materials, one may generally vary the temperature without affecting the amount of the substance present, except if a phase transition is encountered. Therefore, the second term in Equation 7 is normally zero, and the apparent dependence

on the heating rate vanishes except under special conditions. The conclusion of many arguments (9) is that there is no fundamental contradiction between kinetic parameters determined from isothermal and nonisothermal experiments. However, a practical problem of inconsistency between Arrhenius parameters derived from isothermal and nonisothermal experiments still persists.

There are two major reasons (experimental and formal) for the above inconsistency. The experimental reason is that isothermal and nonisothermal experiments are necessarily conducted in different temperature regions. Nonisothermal experiments are generally performed over a wider range of temperatures. For a multi-step process comprised of elementary steps that have different activation energies, the relative contributions of these reactions to the overall rate vary with the temperature. This means that the effective activation energy evaluated by the overall reaction rate will be different in different temperature regions. Therefore, consistent values of Arrhenius parameters can be obtained only when experiments are conducted in the same temperature region. A strict fulfillment of this condition is not possible. However, the temperature region of a nonisothermal experiment can be somewhat narrowed when using slow heating rates. Brown et al (5) recommended the use of slow heating rates in order to reach a better correspondence between the results of isothermal and rising temperature experiments.

The formal reason for the inconsistency of Arrhenius parameters derived from isothermal and nonisothermal experiments originates from the commonly used procedure of force-fitting experimental data to different reaction models. Henceforth, we refer to this procedure as the model-fitting method. A detailed analysis of the use of various model-fitting methods in nonisothermal kinetics can be found in a critical review (29).

There are two fundamental problems with the model-fitting method. The first is that it is not applicable to nonisothermal data. Following this method, the $k(T)$ term is determined by the form of $f(\alpha)$ chosen. In isothermal kinetics, these terms are separated by the very conditions of the experiment [$k(T) = \text{constant at constant } T$]. The determination of the $f(\alpha)$ term is achieved by fitting various reaction models (Table 1) to experimental data. After the $f(\alpha)$ term has been established for a series of temperatures, $k(T)$ can be evaluated. A single nonisothermal experiment provides information on both $k(T)$ and $f(\alpha)$ but not in a separated form. For this reason, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters that compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown kinetic model.

For any set of the reaction models (e.g. those in Table 1), the values A and E determined by the model-fitting method usually show extensive variations for the same sample. An example of this effect is given in Table 2, which shows the

Table 2 Arrhenius parameters computed for the thermal decomposition of ADN at 5°C min⁻¹

	$E/\text{kJ mol}^{-1}$	$\log (A/\text{min}^{-1})$	$-r^a$
1	28.2 ± 0.9	2.1 ± 0.1	0.9478
2	40.0 ± 1.1	3.6 ± 0.1	0.9539
3	63.7 ± 1.7	6.4 ± 0.2	0.9590
4	205.8 ± 5.1	22.7 ± 0.6	0.9647
5	276.9 ± 6.8	30.7 ± 0.8	0.9653
6 ^b	167.8 ± 2.2	18.8 ± 0.3	0.9894
7	36.4 ± 0.6	3.2 ± 0.1	0.9858
8 ^b	51.0 ± 0.7	5.0 ± 0.1	0.9872
9 ^b	80.2 ± 1.1	8.5 ± 0.1	0.9884
10	313.7 ± 5.3	34.4 ± 0.6	0.9832
11	153.2 ± 2.6	16.4 ± 0.3	0.9824
12	147.5 ± 2.9	15.9 ± 0.3	0.9776
13	237.3 ± 6.9	27.5 ± 0.8	0.9523

^a r is the correlation coefficient.^bStatistically equivalent models.

results of fitting 13 reaction models (Table 1) to one set of experimental data (30) for the thermal decomposition of ammonium dinitramide (ADN) using the Coats-Redfern model-fitting method (31). As seen in Table 2, the Arrhenius parameters computed by different reaction models vary by an order of magnitude, which is an unusually large range compared with that of most isothermal experiments (32–35). A pictorial representation of the problem is given in Figure 1, which shows the 13 Arrhenius lines derived from the model-fitting method. All of the lines intersect in a small range of experimental temperatures (because all of the fits describe the reaction rate in that range). However, one can immediately see that the different models provide vastly different predicted rates at temperatures lying only slightly outside the experimental range! A mathematical aspect of the problem has been considered elsewhere (36). Meticulous statistical analysis (37) of the correlation coefficients (r in Table 2) can identify the three best reaction models, which in this example are statistically equivalent. These are identified in Table 2. However, the values of Arrhenius parameters corresponding to these three models also vary significantly. Naturally, such an uncertainty in the kinetic triplet cannot result in reasonable kinetic predictions, nor can it provide useful guidance in drawing mechanistic conclusions (38).

The second fundamental problem is that each application of the model-fitting method results in only a single pair of Arrhenius parameters. In the preceding section, we argued that most solid state reactions are not simple one-step processes and that a combination of serial and parallel elementary steps should

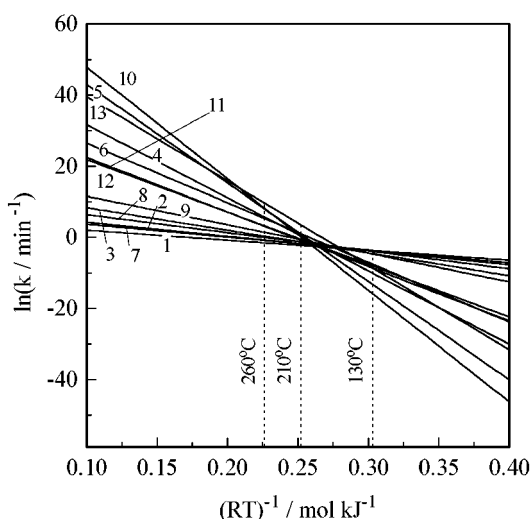


Figure 1 Arrhenius lines plotted by data given in Table 2. The temperature interval of ADN decomposition at $5^{\circ}\text{C min}^{-1}$ is $130\text{--}210^{\circ}\text{C}$.

result in an activation energy that changes during the course of the reaction. However, the argument for variation of E with α is even more general than this, and we must expect that both Arrhenius parameters should be functions of the extent of conversion. To illustrate this point, let us consider the single-step solid state reaction $\text{A} \rightarrow \text{B}$. In general, the activity of A depends on the nature of the molecules that surround it. If A-A intermolecular forces are stronger than A-B forces, then the enthalpy of A will be lower at the initial stages of reaction ($\alpha = 0$) than near the end ($\alpha = 1$). Similarly, the molar enthalpy of pure B ($\alpha = 1$) is lower than those products formed in the initial stages of reaction ($\alpha = 0$). By this simple example, we may conclude that the exothermicity of the reaction increases as a function of α . This situation is illustrated in Figure 2. If the exothermicity is a function of α , then it is also reasonable to conclude that the activation energy is a function of α . The well-known concepts of linear free energy relationships suggest that for this particular example, E should decrease linearly with α . The point of this discussion is not to prove the linearity of this relationship, but rather to stress that in most cases we should not expect the Arrhenius parameters to be constants!

Most solid state reactions are not as simple as the example illustrated above and involve phenomena such as formation of gases at the solid surface, formation of solid solutions, eutectics, and many other effects. The kinetics in these cases will be more complicated than a simple $\text{A} \rightarrow \text{B}$ reaction, so we should

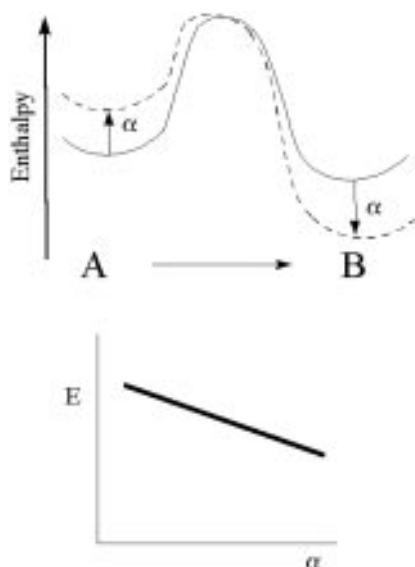


Figure 2 Expected changes in enthalpy and activation energy for a hypothetical single-step reaction. $\alpha = 0$ (solid line); $\alpha = 1$ (dashed line).

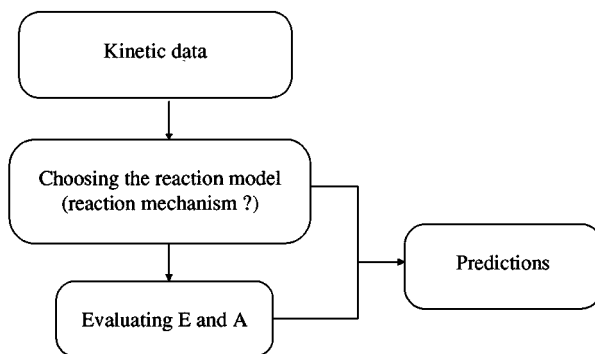


Figure 3 Scheme of the standard approach to kinetic data processing.

expect E to be a function of α for the general case. The model-fitting method is simply not capable of describing this feature of solid state reactions. We are thus forced to conclude that the standard kinetic approach (Figure 3) based on the model-fitting method does not allow one to reach either of the two principal objectives of kinetic analysis.

Unfortunately, this flawed approach has been employed in an overwhelming majority of kinetic analyses, the failures of which sometimes come to light in a quite bizarre form, such as negative (39) or close to zero (40, 41) values of the activation energy, as negative values of the activation entropy for endothermic processes (40, 42, 43), or as a negative estimated number of collisions (44). The flood of inconsistent information produced from nonisothermal data with the model-fitting method provoked an extremely antagonistic attitude toward nonisothermal kinetics as a whole (45). In our view this attitude is justifiable only as it pertains to the use of the model-fitting method in the analysis of nonisothermal experiments.

ISOCONVERSIONAL METHOD AND MODEL-FREE KINETICS

Trustworthy kinetic parameters can only be extracted in a way that is independent of the reaction model. Isoconversional methods are known to allow for model-independent estimates of the activation energy. To use the isoconversional methods, a series of experiments have to be conducted at different heating rates. Then one can apply the isoconversional principle, according to which the reaction rate at constant extent of conversion is only a function of the temperature

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = -E_{\alpha}/R. \quad 8.$$

Henceforth, the subscript α designates the values related to a given value of conversion. This principle is the basis of the isoconversional methods (46–49). The isoconversional method suggested by Friedman (46) uses a differential form of the rate equation, whereas the methods of Ozawa (47) and Flynn & Wall (48) use approximations of the integral Equation 5, which lead to simple linear equations for evaluating the activation energy. Analysis of errors induced by such approximations has been performed by Vyazovkin & Dollimore (49), who introduced a nonlinear isoconversional method to increase the accuracy of evaluating the activation energy.

A model-independent estimate of the activation energy can also be obtained from a single experiment by the temperature-jump method (50), in which sample temperature at a certain moment is changed quickly to another value. The method assumes that the extent of conversion does not vary during the temperature jump, i.e. the change in the reaction rate is proportional to the rate constant alone. Under this assumption, which may hold only if the reaction rate is not too high, one can obtain a model-independent estimate of the activation energy, which obviously corresponds to a given extent of conversion, α . In fact, the

temperature-jump method is an experimental realization of the isoconversional principle. The temperature-jump method was proposed (51) for use in kinetic computations in controlled rate thermal analysis (CRTA) (52). The CRTA experiments are usually performed at low reaction rates, which are kept constant by adjusting the sample temperature.

Although the isoconversional methods are known to allow for model-independent estimates of the activation energy, they are used infrequently because of the problems accompanying their application. One of these is that the original isoconversional methods [e.g. see Friedman (46), Ozawa (47), and Flynn & Wall (48)] do not suggest a direct way to evaluate the preexponential factor or the reaction model. We note, however, that this information can be obtained by approximate techniques (2), discussed below.

The most serious problem is, however, that variation of the Arrhenius parameters with the extent of reaction poses difficulties in the interpretation of the kinetic data. Let us dwell briefly on this problem. The problem of interpretation of the dependence of E_α on α comes from the theoretical concepts that prescribe the activation energy of an elementary reaction step to be constant in gases and in dilute solutions. However, as we mentioned above, we do not generally expect E to be constant for solid state reactions. Furthermore, the kinetics of solid state reactions are known (53) to be sensitive to pressure, temperature, size of crystals, gaseous atmosphere, and other factors that are likely to change during the process. We have to accept the fact that E_α may vary with α .

Revealing the dependence of E_α on α helps to unravel the complexity of a process as well as to gain an insight into its mechanism (2, 3). The sole dependence of the activation energy on conversion is sufficient to reliably predict the kinetics of a process over a wide region of the temperatures (2, 3, 38). The possibility of obtaining information about the mechanism of a process and predicting its kinetics without the knowledge of both the reaction model and the preexponential factor gives rise to the concept of model-free kinetic analysis (2, 54). In other words, the capability of the isoconversional method to determine E_α in a model-free way accomplishes one of the primary goals of kinetic analysis (rate predictions) and provides a new type of clue (E_α) for drawing mechanistic conclusions.

REACTION MECHANISMS

Since the isoconversional methods were proposed, it has been known (48) that the effective activation energy computed for a multi-step process may vary with the extent conversion. Elder (55–59) and Dowdy (60, 61) have performed systematic studies of the isoconversional methods as applied to complex processes comprising competing or independent reactions. Both authors concluded

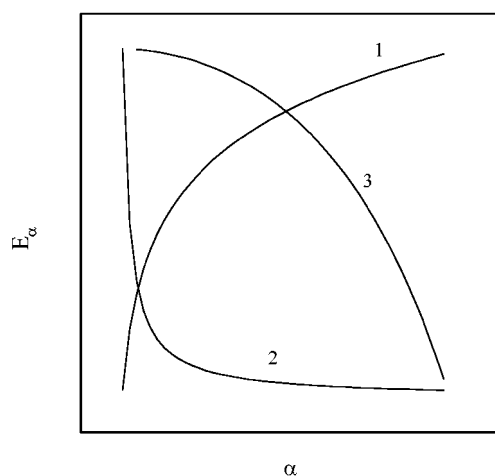


Figure 4 Dependencies of E_α on α characteristic of multi-step processes involving (1) competitive, (2) reversible, and (3) reactions complicated by diffusion.

that the methods are applicable to the study of multi-step processes. Later Vyazovkin & Lesnikovich (62) showed that revealing the dependence of the activation energy on conversion helps not only to disclose the complexity of a process, but also to identify its kinetic scheme. The shapes of the dependence of E_α on α have been identified from simulated data for competing (62), independent (63), consecutive (64), and reversible (65) reactions, as well as reactions complicated by diffusion (66). The most characteristic dependencies are presented in Figure 4. Although the shape of the dependence of E_α on α does not necessarily unequivocally identify the kinetic scheme of a process, it in all instances sheds light on the latter.

An increasing dependence of E_α on α (1 in Figure 4) is found for competing reactions (62), although some independent (63) and consecutive (64) reactions may also exhibit such a dependence. These dependencies have been observed for the thermal decomposition of polypropylene studied using TG (67) and MS (14). Vyazovkin et al (67) explained the observed shapes as resulting from competition between pyrolysis and oxidation taking place in the presence of oxygen. Similar dependencies occurring in the absence of oxygen have been interpreted (14, 67) as competition among decomposition of individual macromolecules and intermolecular associates, which is a mechanism typical of linear polymers (68). These interpretations are likely to apply to the thermal decomposition of many polymers. Increasing dependencies of E_α on α (or on T) have been discovered for the thermal decomposition of polystyrene (68) and

poly(imide siloxane) (69) throughout the entire interval of conversions. Such dependencies are often encountered at the beginning of the thermal decomposition of polymers. Examples of this effect include poly(ethylene terephthalate) (70) ($\alpha < 0.7$), polyethylene (71) ($\alpha < 0.5$), poly(butadieneacrylonitrile-acrylic acid) (72) ($\alpha < 0.25$).

Vyazovkin (64) has examined the dependencies of E_α on α for kinetic schemes involving consecutive reactions. This scheme is applicable not only to the processes for which the existence of consecutive reactions is proven (73–75), but also to processes proceeding with a change from a kinetic to a diffusion regime. Such processes occur frequently in solids that decompose as solid \rightarrow solid + gas. As a surface layer of the solid product grows, diffusion of a gas through it gradually becomes the rate-limiting step of the decomposition. Consideration of the original substance covered by a layer of the product as a reaction intermediate allows a kinetic scheme of consecutive reactions to be applied (66) to the above process. The latter features a characteristic dependence of E_α on α (3 in Figure 4). Similar dependencies have been observed (66) for the thermal decomposition of wood. The crucial role of diffusion in this process is well known (76). Furthermore, analogous dependencies have been established for the first step of decomposition of $(\text{NH}_4)[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ (77) and for the late stage of curing of epoxy resins (3, 78, 79). In the latter example, diffusion-controlled cure has been adequately described (3) when using a kinetic model that accounts for effects of both temperature and conversion on the change in diffusivity.

The kinetics of reactions that proceed through a reversible step have been a source of continuous contradictions. One of the reasons for these contradictions is that kinetic Equation 1 does not account for the pressure dependence of the reaction rate. The failure to account for pressure effects explicitly in the kinetic equations may result in a pressure dependence of the activation energy computed by this equation. Lyakhov et al (80) emphasized that even under isobaric conditions, the Arrhenius plot may be distorted as a result of a nonlinear temperature dependence of the equilibrium pressure. Obviously, any variation of the external pressure may dramatically affect the kinetics of a reversible reaction. For a reaction solid \leftrightarrow solid + gas, an increase in the external pressure enhances the reverse reaction. This shifts the overall process of decomposition to higher temperatures, which usually results in increasing the effective activation energy. A striking example of the pressure-dependent kinetics is the thermal decomposition of calcium carbonate. Because this process is often considered a model one for kinetic studies, it has been extensively examined. Analysis of 168 references (1) showed that while the majority of reported values of the activation energy fit into the interval 120–280 kJ mol⁻¹, the extreme values are 47 and 3825 kJ mol⁻¹. Nevertheless, this span of the activation energies is not

surprising for the substance whose temperature of decomposition changes from 730 K in vacuum to 1070 K in pure carbon dioxide (1).

Changes in temperature also affect the overall kinetics of a reversible process. Vyazovkin & Linert (65) have shown that the decreasing dependence of E_α on α (2 in Figure 2) corresponds to the kinetic scheme of an endothermic reversible reaction followed by an irreversible one. For such a process E_α is limited by the sum of the activation energy of the irreversible reaction and the enthalpy of the reversible reaction at low conversions. At high conversions, E_α is limited only by the activation energy of the irreversible reaction at high conversions (65). The reversible dehydration of crystal hydrates, as well as other processes involving a reversible step, have been found (65) to exhibit these characteristic dependencies of E_α on α . Ironically, the dehydration of calcium oxalate monohydrate [a reaction that is widely used (81–84) in kinetic computations as a reference single-step reaction] also displays (85, 86) these type of dependencies of E_α on α (Figure 5). Similar dependence (E_α decreases from 206 to 97 kJ mol⁻¹) has been found (86a) in CRTA experiments when using the temperature-jump method to evaluate the activation energy. The process is obviously a multi-step reaction with a significant contribution of the reversible reaction. The same conclusion seems to be valid for the dehydration of lithium sulphate monohydrate. This is another process that has been intensively studied (87–90) as a prospective kinetic standard. Not surprisingly,

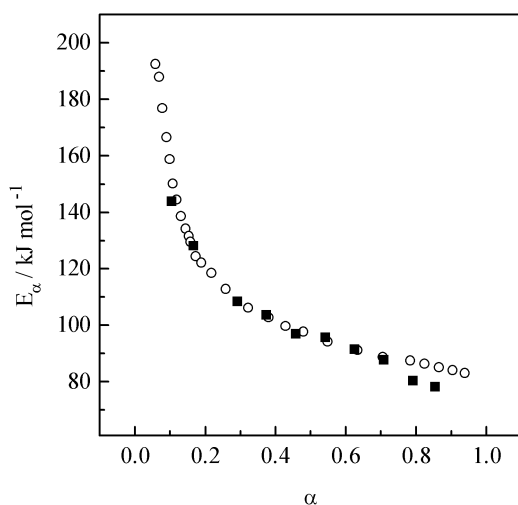


Figure 5 Dependencies of E_α on α for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The curves were plotted using data from References 85 (squares) and 86 (circles).

this process revealed the kinetic behavior very similar to that observed for the dehydration of calcium oxalate monohydrate. In particular, when the isoconventional method was employed to compute the activation energy, decreasing dependencies of E_α on α were detected (87, 88). The average interval of the activation energy variation was 125–75 kJ mol⁻¹ in both articles.

KINETIC PREDICTIONS

As mentioned above, the direct application of isoconventional methods (46–49) does not allow for both identification of the reaction model and a model-independent estimate of the preexponential factor. Therefore, kinetic predictions such as time to reach a specified conversion or reaction rate at some reference temperature cannot be made directly by Equations 1 and 2. Even if the reaction model and preexponential factors are determined in some indirect way, there still is problem with a variation of the activation energy with the extent of conversion. This problem is often overcome by averaging (91–94) E_α over α . Because averaging can only be applied to randomly varying values, averaging of systematic dependencies (91–94) of E_α on α is statistically meaningless. This procedure might be justified when a change in E_α is several percent of the mean value (91, 92), but not when such a change is comparable (93, 94) to the mean value, as in the cases cited in the previous section.

The problem of using isoconventional methods for kinetic predictions can be resolved without averaging E_α and even without evaluating the reaction model and the preexponential factor. To do this we have to assume that the partial (i.e. related to a given conversion) kinetic triplets remain the same when changing temperature. Using this assumption, we can equate Equation 2 (isothermal conditions) and Equation 5 (nonisothermal conditions) with a given conversion. Simultaneous solution of these equations for time yields

$$t_\alpha = [\beta \exp(-E_\alpha/RT_0)]^{-1} \int_0^{T_\alpha} \exp(-E_\alpha/RT) dT, \quad 9.$$

where T_α is an experimental value of the temperature corresponding to a given conversion at the heating rate β . This equation enables the time at which a given conversion will be reached at an arbitrary temperature, T_0 , to be computed. Equation 9 was first derived by Vyazovkin & Lesnikovich (95). Later, similar equations were obtained by Khabenko & Dolmatov (96) and Gimzewski (97). This assumption of conservation of the partial kinetic triplets also permits evaluation of functions $[\alpha(T)]_r$, $[\alpha(T)]_\beta$, $[t(T)]_\alpha$, $[T(\beta)]_\alpha$, and $[\alpha(\beta)]_T$ without the knowledge of the reaction model or the preexponential factor (98).

The absence of both the kinetic model and the preexponential factor in predictive equations means that these components do not induce corresponding

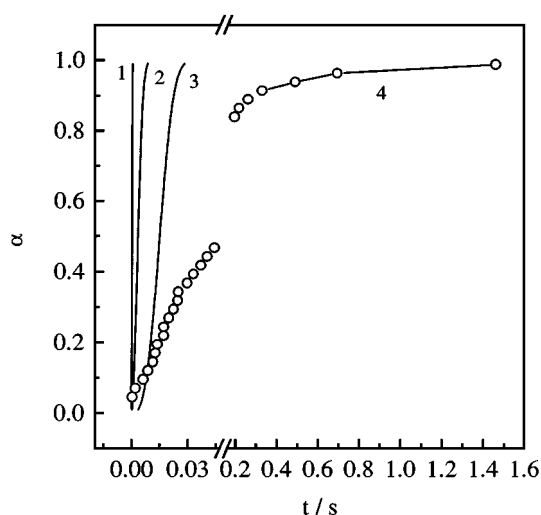


Figure 6 Predicted kinetic curves for the thermal decomposition of ADN. Curves 1, 2, and 3 were plotted by inserting respective kinetic triplets 6, 9, and 8 (Table 2) into Equation 2. Curve 4 is a model-free prediction deduced from Equation 9.

errors when making kinetic predictions. Additionally, the use of the entire dependence of E_α on α in predictions takes into account the complexity of the process. Alternatively a method recommended by ASTM E698 (99) can be used to determine a single value of E in a way that is independent of any particular model. However, the dependence of E on α cannot be obtained in this way, and the evaluation of A involves force-fitting to a first-order reaction model (with the associated error mentioned above). A theoretical analysis of the errors arising in the dependencies of α on t predicted in various ways (including Equations 2, 9, and a method recommended by ASTM) has shown (38) that Equation 9 provides reliable results. Figure 6 shows predicted kinetic curves for the thermal decomposition of ADN (30) at 260°C. The predictions were made using three best kinetic triplets (Table 2) from the model-fitting method and by the model-free method (Equation 9), which accounts for the dependence of E_α on α (Figure 7). An experimental measurement performed by Brill et al (100) shows that at 260°C the time required to the reaction to reach 95% completion is about 0.5 s. Only the model-independent prediction by Equation 9 is in satisfactory agreement with this result. More examples of inaccurate predictions made by the model-fitting method as well as by ASTM E698 method can be found in References 3, 101, and 102. Equation 9 has been successfully used (103) to evaluate the effect of additives on combustion of

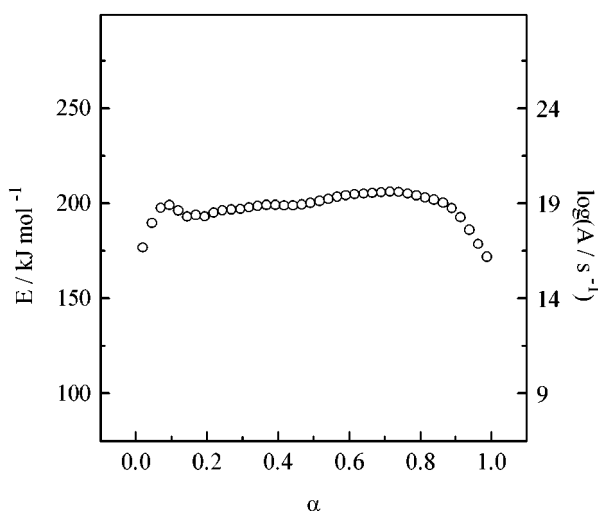


Figure 7 Dependence of the activation energy and the preexponential factor on the extent of conversion for the thermal decomposition of ADN.

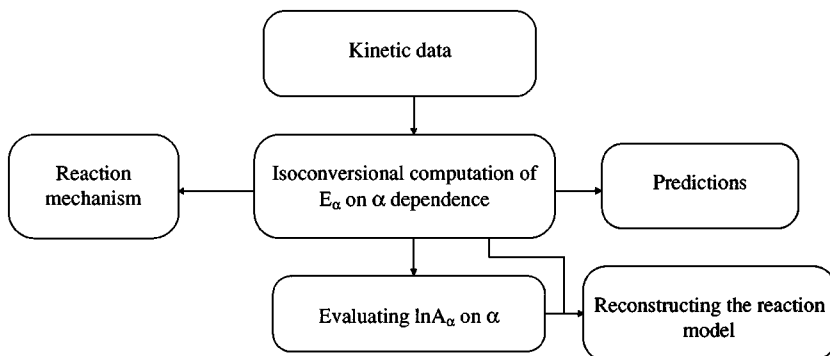


Figure 8 Alternative (model-free) approach to kinetics data processing.

HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocine) as well as to predict the kinetics of epoxy amine cure (2, 3). In each case, the predictions have been confirmed by experimental measurements.

The aforementioned studies have shown that the model-free approach based on the isoconversional method, which is summarized by the flow chart in Figure 8, is capable of accomplishing both of the principal goals of kinetic analysis (rate prediction and mechanistic interpretation). Of course, it is desirable

from a theoretical point of view (and to aid in mechanistic interpretations) to be able to evaluate the preexponential factor and thereby reconstruct the reaction model. Methods of accomplishing this task are discussed in the following section.

EVALUATING THE PREEXPONENTIAL FACTOR AND ISOKINETIC RELATIONSHIPS

The preceding discussion shows that the preexponential factor and the reaction model are not required to accomplish the objectives of the kinetic analysis. However, these components of the kinetic triplet can be evaluated. After a model-independent estimate of the activation energy has been obtained, several methods (104–106) can be used to determine the reaction model and preexponential factor. It should be emphasized that by any of these methods the preexponential factor can be evaluated only by assuming that the reaction model has a particular functional form. In other words, these methods do not allow for a model-independent estimates of the preexponential factor.

A model-independent estimate of the preexponential factor can be obtained (107, 108) through the use of an artificial isokinetic relationship (IKR). Generally speaking, an IKR manifests itself both as a common point of intersection of Arrhenius lines

$$\ln(k_{\xi}) = \ln(k_{\text{iso}}) - E_{\xi}/R(T_{\text{iso}}^{-1} - T^{-1}) \quad 10.$$

(where k_{iso} and T_{iso} are, respectively, the isokinetic rate constant and the isokinetic temperature) and as a linear correlation of Arrhenius parameters (the so-called kinetic compensation effect)

$$\ln A_{\xi} = a + bE_{\xi}, \quad 11.$$

where $a = \ln(k_{\text{iso}})$ and $b = -(RT_{\text{iso}})^{-1}$ are coordinates of the intersection of point of Arrhenius lines, and the subscript ξ refers to a factor that produces a change in Arrhenius parameters. A concise review of IKRs encountered in solid state kinetics can be found in Reference 109. As was shown in Figure 1, the Arrhenius lines resulting from the model-fitting method intersect at (nearly) one point. This means that Arrhenius parameters related to different reaction models will show a linear correlation (cf Arrhenius parameters given in Table 2)

$$\ln A_j = c + dE_j \quad 12.$$

(where j is an index that specifies each reaction model). Once the correlation parameters c and d have been evaluated, the E_{α} values are substituted for E_j in Equation 12 to estimate the corresponding $\ln A_{\alpha}$ values. Obviously, the

resulting $\ln A_\alpha$ values will depend linearly on E_α . Such dependencies have been observed (110, 111). Figure 7 displays the values of $\log A$ estimated by this method for the thermal decomposition of ADN. It should be noted that this approach is based on a completely artificial IKR derived from erroneous results of the model-fitting method. However, whether the reaction model is false or true, the Arrhenius parameters determined by it fit into a common straight line. The resulting IKR thus allows for a determination of the true value of the preexponential factor even if the true model is not included in the analysis.

Real IKRs also exist. Any change in the physical conditions under which reaction occurs can, in principle, affect the activation energy and preexponential factor obtained from the kinetic analysis. A simple example is that the rate and temperature dependence of a thermal decomposition reaction that converts a solid to gaseous products will likely depend on the size distribution of the crystallites (i.e. the ratio of surface area to volume of the sample). Brill et al (112) have recently discussed kinetic compensation effects observed in the thermal decomposition reactions of high explosives. Obviously, the use of the model-fitting method to investigate real IKRs is questionable (113) because the method itself generates an artificial IKR. However, the use of isoconversional methods, in combination with the procedure outlined above for evaluating the preexponential factor, provides a useful opportunity (113) to detect real IKRs. A necessary condition for an IKR to be real is the ability of the ξ factor to affect the temperature dependence of the reaction rate. If the ξ factor does not satisfy this condition (e.g. if it merely denotes different models used in the analysis of one data set), then only an artificial IKR (108) may result.

Linert & Jameson (114) have suggested that the occurrence of a real IKR may be associated with a resonant vibrational energy exchange between reactants and their molecular environment. They point out that the characteristic frequency of this interaction

$$\nu_{\text{iso}} = k_{\text{B}} T_{\text{iso}} / \hbar \quad 13.$$

(where k_{B} and \hbar are the Boltzmann and Planck constants, respectively) falls in the mid- to far-infrared region of the spectrum for many reaction systems (114, 115). In many cases, particular vibrational frequencies of the system can be identified that closely match the experimentally determined value of ν_{iso} . However, it has yet to be shown that there is a direct causal relationship between the vibrational frequency and the observed variations in kinetic parameters.

RECONSTRUCTING THE REACTION MODEL

Having determined the values of the preexponential factor and the activation energy, one can reconstruct the reaction model numerically (2, 54). The integral

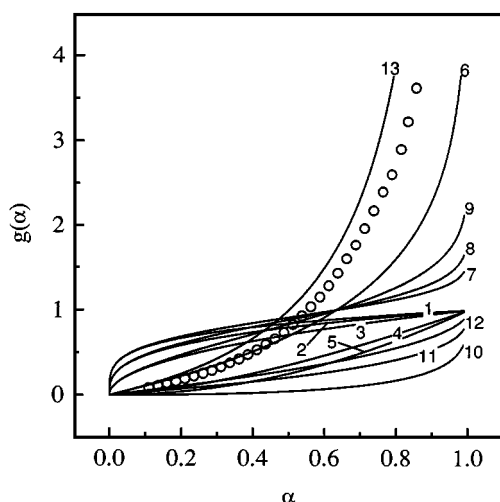


Figure 9 Dependence of $g(\alpha)$ on α for the models in Table 1 (solid curves) and for the experimental data (open circles) for the thermal decomposition of ADN.

form of the reaction model, $g(\alpha)$, can be reconstructed by substituting model-independent estimates of E_α and A_α into Equation 5. Figure 9 shows such a dependence for the thermal decomposition of ADN. Alternatively, the differential form of the reaction model, $f(\alpha)$, can be reconstructed using the expression

$$f(\alpha) = \beta(d\alpha/dT)_\alpha [A_\alpha \exp(-E_\alpha/RT_\alpha)]^{-1}. \quad 14.$$

An explicit form of the reaction model can then be identified by comparing proposed models (e.g. those in Table 1) with the numerically determined reaction model, $f(\alpha)$, or its integrated form, $g(\alpha)$. The interpretation of such a reconstructed reaction model is straightforward only for a single-step process. An indication of this situation might be if E_α were found to be independent of α . However, we stress that even for single-step reactions one may not generally anticipate that this will be the case.

EFFECT OF TEMPERATURE DEVIATIONS ON THE KINETICS

Whatever the prescribed heating program is, the actual variation of the temperature inside the reaction system tends to deviate from it, primarily because of the thermal effects of the reactions. Experimental measurements performed on $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and on a mixture of CaCO_3 with $\text{Ca}(\text{OH})_2$ have shown (116)

that the endothermic effects of the thermal decomposition of these substances make the actual sample temperature deviate from the prescribed linear program by as much as 10 K. Obviously, such deviations have a profound effect on the apparent reaction kinetics (117–119). In addition to disguising the real kinetic parameters, they invalidate the use of equations based on the assumption that a prescribed heating program holds. We have recently found (120) that the temperature deviations may result in an incorrect dependence of the activation energy on conversion. The use of this erroneous dependence would lead to incorrect kinetic predictions as well as to irrelevant conclusions about the reaction mechanism. The temperature deviations can be minimized by using small samples, slow heating rates, and/or inert materials for heat dilution. The use of the CRTA method (52), which permits one to keep the reaction rate slow, is another opportunity. In many cases, however, these methods are inapplicable, ineffective, or simply challenging from an experimental perspective.

In cases where experimental techniques fail to eliminate temperature deviations, kinetic computations must be based on the actual variation of the sample temperature. Such computations are feasible with the help of the advanced iso-conversional method (120), which is applicable to an arbitrary variation in the temperature. The method combines the isoconversional principle of evaluating the activation energy with numerical integration of the differential rate equation

$$(d\alpha/dt)_\alpha = \left[f(\alpha) A \exp \left(\frac{-E}{RT(t)} \right) \right]_\alpha \quad 15.$$

over a set of the actual time-dependent temperature distributions $T(t)$ of the sample.

CONCLUSIONS

Two of the features of solid state reactions that make kinetic analysis difficult are their localized character and the fact that the environment of the reactants changes during the course of the reaction. This is distinctly different from the case of reactions in the gas phase or in dilute solutions, where each molecule is surrounded by a constant environment (vacuum or solvent) throughout the entire transformation. Reactions of pure liquids also suffer from a change in environment, but the fluid character makes the entire sample essentially homogeneous such that the local phenomena that play such a prominent role in solid state kinetics (e.g. cracks, defects, and trapped radicals) are essentially absent in liquids.

The widely used model-fitting method is generally doomed to fail for two reasons. First, the true functional form of the reaction model is almost never known, and the Arrhenius parameters determined by the method are skewed to compensate for errors in the model. Second, the model-fitting method is only capable of determining a single set of kinetic parameters for the overall

reaction. In contrast, we may generally expect that the activation energy and preexponential factor change during the course of reaction. The model-fitting method is incapable of describing this.

The isoconversional method, though somewhat more demanding from a computational point of view, permits a model-free evaluation of E_α by making the assumption that this quantity is only a function of α and not, for example, of the heating rate. This method allows reliable prediction of the reaction rate outside the experimental range of temperatures, subject only to the validity of the Arrhenius expression. Examination of the functional form of E_α can be used to draw some mechanistic conclusions. If desired, the method can be extended to include analysis of $\ln A_\alpha$ and numerical reconstruction of the reaction model. These functions may also be helpful for elucidating the reaction mechanism. Because the isoconversional method is model-free, the method avoids the problems associated with generating an artificial IKR, and therefore offers a reliable way for detecting real IKRs associated with variations in sample preparation and reaction conditions.

As representative paradigms of solid state reactions emerge and the methods of kinetic analysis become increasingly sophisticated, we expect that a convergence of theoretical solid state kinetics and practical kinetic analysis will occur. At that stage, it will become easier to utilize kinetic data for gaining a deeper insight to the mechanistic details of reactions in the solid state.

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