

Special Review

**TEMPERATURE DEPENDENCE OF THE RATE OF REACTION
IN THERMAL ANALYSIS**

The Arrhenius equation in condensed phase kinetics

J. H. Flynn

SCIENTIFIC THERMAL RESEARCH & DATA ANALYSIS (STRDA) 5309 IROQUOIS ROAD,
BETHESDA, MARYLAND 20816, USA

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Special problems are encountered in modeling the temperature dependence of the kinetics of heterogeneous, condensed phase systems. In the division of the model for the reaction rate into two parts, a) $f(\alpha)$ which is physical (translational) and b) $k(T)$ which is chemical (vibrational), complications arise in defining the temperature dependence of part a) which may take various mathematical forms and then in coupling it with the Arrhenius temperature dependence of part b). The role of $f(\alpha)$ in thermal analysis systems is discussed. The concept of rate-controlling step is applied to the simplification of the temperature dependent term. The significance of the compensation effect in these systems is described and an heuristic rationalization for it is suggested. Maximum practical temperature ranges for thermal analysis experiments and the effect of temperature measurement imprecision on obtaining meaningful Arrhenius parameters are discussed. The WLF and other equations used to describe the temperature dependence of $f(\alpha)$ are not found to couple compatibly with the Arrhenius equation.

This paper discusses many of the special problems which one faces in the modeling of the temperature dependence of the kinetics of the reactions in crystalline and amorphous condensed phase systems. It is, in the greater part, based on a lecture given and published at the Fifth Seminar in Memory of Stanislaus Bretsznajder [1].

It is convenient to divide the mathematical model for the rate of a chemical reaction into two parts. a) The first is an expression which describes the ability of molecular species or functional groups to come in contact with one another so that they will have the potential to exchange energy, electrons or atoms, and/or, after such an exchange, to separate to form intermediates

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and products, and we designate this expression, $f(\alpha)$. b) The second part is an expression which describes the ability of these "reacting species" in a), once they meet, to overcome any free energy barriers which stand in the way of the reaction taking place. This seems to be a valid way to separate the two parts. Part a) is often a physical process (translational) and, when temperature dependent, can only sometimes be modeled by the Arrhenius equation. Part b), being chemical in nature (vibrational), is nearly always temperature dependent and usually is modeled by the Arrhenius equation.

There is one ambiguity in making this separation. The most common form of the Arrhenius equation used for the temperature dependence of the rate of reaction is

$$k = A \exp(-E/RT) \quad (1)$$

where k is the rate constant, A , the preexponential factor, E , the energy of activation, R the gas constant, and T , the absolute temperature. When Eq. (1) is developed for an elementary chemical process, A represents the "frequency factor" in collision theory or the "entropy" part of the free energy of activation in transition state theory. In the complex reactions of thermal analysis, it is not clear at what point one can distinguish per se between the functions for the macroscopic motions of reactant and product species in $f(\alpha)$ and the functions for microscopic motions along the reaction coordinate contained in frequency factor or transition entropy, A . However since it is impossible to separate $f(\alpha)$ and A by analysis of experimental kinetics data, the question is academic as the actual separation would only need to be taken into account during a complete and detailed modeling of the reaction kinetics.

Role of $f(\alpha)$ in thermal analysis systems

Before discussing the applicability of the Arrhenius expression to these systems, it is instructive to discuss the role of part a) in the kinetics of the condensed phase systems of thermal analysis. This is necessary since the mathematical form for the model for part a) (which is usually simple and uncomplicated for homogeneous systems) is often both complex and obscure for condensed phase systems. Even more to the point, these "collisions" in the solid phase are often strongly dependent upon temperature. This temperature dependence may even be of the Arrhenius type. An example of this case is the Fickian diffusion of reactants in polymers well above their

glass transition. In some examples to be described later other expressions for the temperature dependence may be appropriate. Any temperature dependence of part a) must be coupled with the Arrhenius temperature dependence of part b) in the formulation of a mathematical model for the temperature dependence of the overall reaction rate.

The situation is usually quite simple for the kinetics of homogeneous reactions. It is assumed in the mathematical modeling of part a) that the reaction rate is proportional to the partial pressures of the reacting species for homogeneous gas phase reactions and proportional to the concentrations of reactants for homogeneous reactions in solution. Some sort of mild m th power ($0 < m \leq 1$) temperature dependence is often postulated for the model from the kinetic theory of gases for the collisions of these species (or for the entropic term of the statistical mechanical model for the transition state) but this temperature dependence is usually ignored in comparison to the exponential temperature dependence of the Arrhenius equation.

However, even if there are no heterogeneous effects such as dust, walls, etc., catalyzing reactions in gaseous and solution systems, pressures and concentrations are not completely satisfactory experimental variables to use in describing the function for degree of advancement or extent of reaction in the rate equation which is the term we have already designated as $f(\alpha)$. One has to take into account "nonideality" resulting from molecular attraction, finite size of atomic species, solvation and other complicating factors. This is sometimes accomplished by defining a function called "activity" to replace pressure or concentration terms in the equations for $f(\alpha)$. In homogeneous systems this activity or its proportionality factor to the measured physical property, the activity coefficient, takes into account the departure from ideality of the real reaction system.

The concept of activity may be useful at least in the discussion of the kinetics of heterogeneous condensed phase systems, if not in the actual formulation of their equations. Certainly, in many cases, the reaction rate will be dependent upon the mobility of at least one of the reacting or produced species. Even in dissociation reactions for crystalline solids in which low molecular weight product gases such as water or carbon dioxide may diffuse easily from the system, the initiation step often involves the "random flight" or "fractal kinetics" movement of imperfections or vacancies through the crystal lattice (often resulting in Avrami-type kinetics behavior). However, assessment of the utility of such an activity function model must await a discussion of the problems involved in the mathematical modeling of the kinetics of the condensed phase.

It is instructive to look at a few examples of the types of complexities that can be expected in the kinetics of these systems. Reaction rate is measured from changes in an extensive property of the system such as mass, enthalpy, volume, etc. This discussion is framed in terms of mass as it is a measured property which is often assumed to be relatable to the extent of reaction function in setting up equations for the kinetics of condensed phase systems, and mass is used widely in thermal analysis kinetics by substituting mass for pressure or concentration in the equations which are traditionally used to represent the kinetics of homogeneous systems. (Mass can be substituted successfully for concentration since the density of the condensed phase changes very slowly with changing temperature.) The assumption that the rate is proportional to a function of the mass (which may contain a proportion of active groups) produces satisfactory results for some systems, for example: 1) polymerization (cure) and depolymerization (degradation) reactions often take place in the liquid state (albeit quite viscous) by free radical chain mechanisms whose stationary state approximations yield equations related to the mass of the substrate, 2) vaporization of a liquid or evaporation of a volatile substance from a solid will often follow the Langmuir molecular effusion equation and be proportional to the exposed surface area which may be mass dependent as in the case of a spherical drop, 3) in the analysis of fluorescence glow curves, the number of electrets is proportional to the mass, 4) many cases of diffusion from a polymer matrix depend on the mass of the diffusant in the material, and 5) other cases of surface reactions may be related in some way to the mass such as contracting spheres or cylinders or nucleation (Avrami) models for the kinetics. Of course, there are many other cases.

However equations in which $f(\alpha)$ is assumed to be a function of mass can be a very poor choice in that they assume that each atom or molecule in the bulk of the reacting material or on its surface has the same activity for reaction. This is not the case for many heterogeneous reactions as, for example, in the case of surface catalysis where different surface sites have differing catalytic activity and the more active sites get used up first. In another case, the partial pressure of a gas in contact with the substrate may be the crucial factor in the defining of activity. Hence specimen mass often may not be the significant factor in the formulation of the rate equation.

In other cases, physical changes in the specimen may be the deciding factor as to whether or not a reaction will occur. Melting, softening, gelling, glassing, or reaching a region of miscibility are temperature-dependent phenomena and the mobility of reactants and products may depend upon the development of such events. Sintering is a temperature-dependent

phenomenon which can destroy catalytic activity. The activity of the reactants in such cases may be related to the mass of material, but the crucial, rate-controlling event may be the occurrence of the temperature-dependent physical transformation which is not mass dependent. Thus, to take an extreme case, melting with decomposition, at one temperature the activities of the reactants, held in a rigid lattice, are essentially zero, and, at a slightly higher temperature, above the melting point, their activities suddenly become very great, and the rate equation may need to include a large step function in temperature at that point to represent this increase.

Coupling of Arrhenius equations - rate controlling step

Therefore, from the above discussion, it is obvious that the $f(\alpha)$ function for each heterogeneous reaction system may include its own unique form of temperature dependence. In many cases, the temperature dependence may be easily separated from the remainder of $f(\alpha)$ and incorporated into b), to form the temperature dependent term in the rate equation which we designate as $k(T)$ (the overall or "global" rate constant). In some of these cases, the temperature dependence of $f(\alpha)$ will have an exponential (Arrhenius) form. For example, often material diffusion or viscous flow has an Arrhenius temperature dependence. Here the temperature terms may be coupled mathematically so that a single overall global energy of activation parameter will satisfy the temperature dependence of the rate of reaction. This case is mathematically indistinguishable from those in which $k(T)$ is composed of several elementary rate constants due to a complex kinetics mechanism for the chemical reaction. The two cases for which an overall global energy of activation may be obtained from coupled Arrhenius equations are:

a) The Arrhenius terms are present as a product, e.g., $(\exp(-E_1/RT) \dots \exp(-E_i/RT) / \exp(-E_j/RT))$. Stationary state solutions of free radical chain reaction kinetics such as in polymer cures or degradations can often be reduced to this form. Other reactions whose equations include a temperature dependent equilibrium constant or a diffusion constant also can be of this form. These cases yield a global E/R and $\ln A$.

b) An algebraic summation of Arrhenius terms - $a \exp(-E_a/RT) + b \exp(-E_b/RT) + c \exp(-E_c/RT) + \dots$. Most equations for the kinetics of complex reactions in solids are of this type. This includes cases of reversible, autocatalytic, independent, parallel and consecutive reactions. There can be a number of temperature dependent events separate from those involved in overcoming the free energy barrier along the chemical reaction coordinate;

for example, melting can be followed by diffusion of reactants, the chemical reaction and finally by the diffusion of products.

There is no way that a single Arrhenius expression can be an exact equivalent of such an arithmetic series of individual Arrhenius terms as in case b). However, the concept of "rate-controlling step" [2] allows one to approximate the temperature dependence by using a single energy of activation. For example, if one of a series of consecutive processes goes at a much slower rate than all of the others then the overall rate will be dependent primarily upon its kinetics parameters. (N.b., the rate-controlling step is not necessarily the one with the slowest rate, see ref [2]; also the "rate-controlling step" concept is quite arbitrarily extended in this present paper to apply to systems which are composed of sets of "nonelementary" reactions.) The "rate-controlling step" concept saves the day in the analysis of the kinetics of many complex solid phase reactions. Even though the rate-controlling step may change as the reaction proceeds or as the experimental conditions change, appropriate rate constants and energies of activation often can be calculated for the one reaction which is controlling the rate in its particular region of dominance.

(It should be noted that, in these discussions, the cases of the kinetics of composite systems for which two or more completely independent reactions are taking place in the same temperature range are not included. Such systems require a completely different kind of mathematical analysis to attempt to deconvolute the component processes and separate their kinetics parameters.)

Probably the most important rate-controlling step in thermal analysis is diffusion. If it was shown that the rate constant will be proportional to the diffusion constant for homogeneous "self stirred" reactions by Smoluchowski [3] and this is probably also the case in many heterogeneous systems.

(There is another form of temperature dependence of the rate which is often successfully applied to viscoelastic properties and transformations in the glass transition region - the WLF or VTF equations which will be discussed later.)

The Arrhenius equation

When Arrhenius proposed his equation for the temperature dependence of the rate of reaction one hundred years ago [4], he based his arguments upon thermodynamic considerations. It was not until later that gas phase kineticists brought up the notion of "tails of Boltzman energy distribution" as

a rationalization of the equation based on kinetic theory of gases. The pendulum swung back when transition state theory based on a statistical mechanical development was introduced over fifty years ago [5]. It is this latter approach that will be evoked later on in the discussion of the "compensation effect".

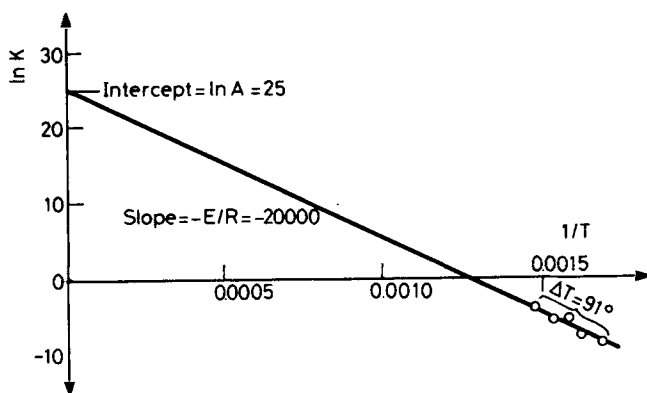


Fig. 1 An Arrhenius plot of $\ln k$ vs. $1/T$

Equation 1), the Arrhenius equation, is used in its logarithmic form as in Eq. (2) for calculating the parameters, $\ln A$ and E/R .

$$\ln k = \ln A - (E/R)(1/T) \quad (2)$$

Therefore, when this equation describes the temperature dependence of the rate, a plot of $\ln k$ against $1/T$ as shown in Fig. 1 will result in a reasonably straight line whose slope will be $-E/R$ and whose intercept at infinite temperature will be $\ln A$. Equation (2) may be multiplied by T to obtain [6]

$$T \ln k = (\ln A)T - (E/R) \quad (3)$$

and a plot of $T \ln k$ against T will have a slope of $\ln A$ and an intercept at zero temperature of $-E/R$ as shown in Fig. 2. It can be seen from these figures that even for an extended experimental temperature range (91 degrees), the slope and intercept are calculated from data covering only a short segment of the total curve. However, if one uses the same sort of

regression analysis on the same sets of (k, T) data, then, of course, the two plots will yield identical values for the two parameters, $\ln A$ and E/R . The only advantage of one equation over the other is that a graph of Eq. (2) gives an easier visual comparison for variations in $\ln A$ for a set of Arrhenius curves while a graph of Eq. (3) allows a better visual comparison for variations in E/R . (This is true only if the whole extrapolation range of temperature is plotted as in the above figures. If only the experimental temperature range is plotted, then large changes in E/R can be better observed from variations in the slope of Eq. (2).)

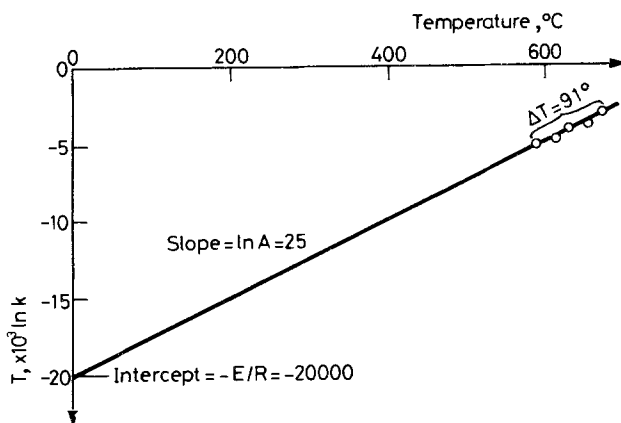


Fig. 2 An Arrhenius plot of $T \ln k$ vs. T

However, Eqs (2 and 3) are not trivially introduced here as they serve to emphasize the complete interdependence of the two Arrhenius parameters, E/R and $\ln A$. This is a basic property of the Arrhenius equation and this relationship between E/R and $\ln A$ has been long recognized as a *raison d'être* for the "compensation effect" which is discussed next. The mathematical foundation for this interdependence has been analyzed and discussed in papers which are briefly reviewed later.

Compensation effect

Before discussing the Arrhenius equation, we will define another equation based upon it. The compensation effect equation is defined as a linear

relationship between the Arrhenius parameters, $\ln A$ and E/R , for a series of "similar" reactions,

$$\ln A = a E/R + b \quad (4)$$

$$\text{so that, } \ln k = a(E/R) + b - (E/R)/T. \quad (5)$$

$1/a$ is called the "isokinetic temperature", T_{iso} , and b is equated to $\ln k_{\text{iso}}$ which is called the isokinetic rate constant, thus,

$$\ln A = E/RT_{\text{iso}} + \ln k_{\text{iso}} \quad (6)$$

or,

$$\ln k/k_{\text{iso}} = E/R (1/T_{\text{iso}} - 1/T). \quad (7)$$

Any case in which there is a "compensation effect" between $\ln A$ and E/R values which were obtained from experiments upon identical specimens studied under the same conditions must be a false effect and either the result of scatter of the experimental data, misapplication of kinetics equations, or errors in the experimental procedures. Most often such a false or "pseudo" effect is explained by the unavoidable scatter of imprecisely calculated slope and intercept (E/R and $\ln A$) values about the mean value of the measured $\ln k$ range. Papers discussing the mathematical correlation dependence for E/R and $\ln A$ have been reviewed by Sestak [7] and the sensitivity of scale values of Arrhenius coefficients, especially for decomposition reactions of the type, A (solid) = B (solid) + C (gas), have been thoroughly analyzed by Pysiak [8].

"Real" compensation effects occur only with Arrhenius parameters from experiments on similar reactions (such as the hydrolysis of a series of homologous esters) or reactions in which the substrate has been chemically or physically modified in a systematic manner (such as reactions on a series of differently pretreated catalysts). The criteria for identifying cases of real compensation effects have been rediscussed in recent literature [7, 9-11] and in older papers [12-14]. As pointed out by Agrawal [9], the criterion for a true compensation effect is the convergence of Arrhenius curves to a single point ($\ln k_{\text{iso}}$, $1/T_{\text{iso}}$).

A heuristic explanation for the existence of this relationship is suggested from transition state theory where the rate constant for an elementary chemical reaction is given by

$$\begin{aligned} \text{rate constant} &= K(k'T/h) \exp(-\Delta F^*/RT) = \\ &= K(k'T/h) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT). \end{aligned} \quad (8)$$

where K is the "transmission coefficient", k' is the Boltzmann constant, h is the Planck constant, and ΔF^* , ΔS^* , and ΔH^* are the Gibbs free energy, the entropy and the enthalpy of activation. Thus the Arrhenius preexponential term, A , can be associated with the entropy of activation, $K(k'T/h) \exp(\Delta S^*/R)$ and the Arrhenius E/R with the enthalpy of activation ($\Delta H^*/R$). The complex heterogeneous reactions which comprise the mechanism of many condensed phase kinetics systems are certainly not "elementary" but the same laws of thermodynamics hold for them. It has been suggested that the rate-controlling step of a reaction sequence is the one which contributes most to the free energy of activation, ΔF^* . For complex systems, the potential energy surface in the transition region will be altered by minor changes in the physical or chemical properties of the substrate. However, when differing reaction paths are competitive with one another, they will all have approximately the same value for ΔF^* . On the other hand, in these cases, the ratio of the entropy contribution, ΔS^* , to the enthalpy contribution, ΔH^* , may increase considerably as the mechanism shifts from one controlled by a chemical reaction to one controlled by a physical one so that since

$$\Delta H^* + T\Delta S^* = \Delta F^* = \text{constant}. \quad (9)$$

This variation in $\Delta H^*/\Delta S^*$ at constant ΔF^* is, of course, just a statement of the compensation effect. Similar arguments have been used in the past to explain the presence of the compensation effect for organic reactions in solution [15].

The temperature range in thermal analysis kinetics

It should be quite simple to determine whether the Arrhenius equation does or does not apply to a particular set of kinetics data. However, in actual cases, it is difficult to decide if the data are sufficiently reliable to give unique values for its parameters. There is no reason why several experiments on the same substance under identical procedural conditions should show a compensation effect and, as mentioned above, it has been suggested that, in such a case, the "pseudo" compensation effect is a demonstration of

an unavoidable random error in the determination of the slope and intercept of an Arrhenius plot. It is true that many calculations of Arrhenius parameters are performed over insufficiently wide ranges of rate and temperature and, for such cases which result in a large scatter of E/R and $\ln A$ values, a "pseudo" compensation effect is inevitable.

The range of the variable, k , which can be measured by thermal analysis experiments can be estimated. Fast reaction rates in thermal analysis become heat and/or material flow dependent so time constants of less than 30s are certainly untrustworthy. This value will serve as an upper limit for the rate constant, k . Modern TG or DCS instruments have very stable base lines so that a reaction can be followed over a period of a week or 604, 800 s which may be used as a lower limit for k . Thus one can calculate a maximum practical experimental temperature range in Table 1, where temperatures are obtained from the equation, $1/T_i = (\ln A - \ln k_i)/(E/R)$, for $k_1 = 1/30$ s, $k_2 = 1/604, 800$ s and several values of $\ln A$ and E/R which are typical for polymer degradation reactions.

The temperature ranges (T_2-T_1) in Table 1 from 133 to 182 K show that a reaction temperature range of at least 100 degrees may be obtained by assiduous kinetics studies. A 100 degree range of temperatures will cover only ten to twenty percent of the total temperature (or $1/T$) scale in most thermal analysis experiments (as illustrated in Figs 1 and 2). Thus this 100 degree experimental temperature range may be necessary for obtaining a reliable fit to the Arrhenius equation. Week long experiments may not be "practical" in many applied studies. However, certainly E/R and $\ln A$ values calculated from experiments covering a range of less than fifty degrees are of doubtful scientific value. Also, large experimental temperature ranges are necessary to expose changes in reaction mechanism which manifest themselves through changes in the slope of an Arrhenius plot [16].

At the constant rate increment in Table 1, the percentage change in temperature depends on the magnitude of $\ln A$ and is independent of E/R , while the reciprocal temperature range depends on E/R and is independent of $\ln A$. Obviously a wider experimental temperature range is realizable from reactions with low energies of activation than from those with high energies [17].

Temperature imprecision

Temperature imprecision is probably the greatest source of error in thermal analysis experiments. Temperature imprecision tends to increase with

increasing temperature. If one assumes a constant percentage error in T (or $1/T$), then a 4 - 6 K temperature range would give the same imprecision in Arrhenius parameter calculation as would temperature ranges of 40 - 60, 400 - 600 or 4000 to 6000 K. On the other hand, if the imprecision in temperature is constant throughout the temperature scale then the same imprecision would be obtained for temperature ranges of 4 - 104, 40 - 140, 400 - 500, 4000 - 4100, etc. degrees. Each experimental apparatus will have its individual temperature error distribution which will lie somewhere in between constant error and constant percentage error so it is impossible to construct a typical temperature error model for Arrhenius plots.

Table 1 T_1 and T_2 Calculated for $k_1 = 1/30$ s, $k_2 = 1/604, 800$

$\ln A$ ($\ln 1/s$)	E/R (K)	T_2 (K)	T_1 (K)	$(1/T_1 - 1/T_2)$ (1/K)	$(T_2 - T_1)$ (K)	% change in T (and $1/T$)
35	30.000	781.2	621.0	0.0003301	160.15	22.8
35	25.000	651.0	517.5	0.0003961	133.47	22.8
30	25.000	748.5	577.4	0.0003961	171.06	25.8
30	20.000	698.8	461.8	0.0004952	136.94	25.8
25	20.000	704.2	522.1	0.0004952	182.05	29.8

Thermal analysis experiments performed at changing temperature such as at constant heating rates should cover an equally wide range of $1/T$ values if Arrhenius parameters are to be calculated. Again, this requires considerable patience since experiments at fast heating rates where thermal and material diffusion may be dominant factors are not acceptable. However, large experimental temperature ranges can be obtained. For example, values for reaction rates have been measured for temperature ranges of greater than 100 degrees during an investigation of the thermal degradation of polymers at heating rates from 0.0001 to 0.1 degrees/sec (9 deg/day to 6 deg/min) [16]. The imprecision in the measurement of the temperature of a specimen is usually greater during programmed temperature change experiments than isothermal ones. However, at constant heating rate, such errors tend to be systematic. Systematic errors in temperature measurement have much less effect than random errors upon the precision of E/R and $\ln A$ values calculated for the Arrhenius equation.

The WLF equation

Another type of exponential temperature dependence is successfully applied to the kinetics of glass and other second order physical transitions and viscoelastic parameters. Often these transformations are analyzed by a dynamic oscillatory technique such as Dynamic Mechanical Analysis, DMA, or Dielectric Thermal Analysis, DETA. A term " a ", the shift factor (which is proportional to the rate constant), is used for systems in which shifts in the reaction rate are obtained by varying the oscillating frequency. A logarithmic plot of a viscoelastic property at temperature T_1 can be obtained from a plot at another temperature T_2 by shifting the curve along the logarithm time (or logarithm frequency) axis an amount equal to $\ln a(1, 2)$, (the time-temperature superposition principle). The temperature dependence of $\ln a$ is often fitted to the Vogel-Tammann-Fülcher equation [18],

$$\ln a = \ln A + 1/b(T-T_\infty), \quad (10)$$

or its equivalent, the Williams-Landel-Ferry (WLF) equation [19],

$$\ln a = -c(T-T_0)/(c' + T - T_0). \quad (11)$$

The WLF and Vogel equations for temperature dependence are applied to viscoelastic processes occurring at temperatures between T_g and $T_g + 100$ K [20]. Therefore when, as is often the case, the increase in activity of a reacting species depends on a change in a viscoelastic property, temperature dependent functions as in Eqs (10 and 11) should be considered. These types of kinetics behavior with respect to temperature are interpreted in terms of the Doolittle free volume expression.

In the fitting of temperature dependence of the rate for thermal analysis systems in which both viscoelastic and chemical processes are involved, either the Arrhenius or the WLF equation has been applied. The two equations do not lend themselves to coupling to form a reasonably simple analytical function. Therefore analysis has been limited to cases in which either the viscoelastic or the chemical process is rate-controlling.

Conclusions

Formally setting up separate temperature functions for the $f(\alpha)$ and $k(T)$ and combining them to produce an overall function for temperature

dependence of the rate may be a helpful routine for developing a satisfactory model for the kinetics of thermal analysis systems. However, in the development of realistic models of $f(\alpha)$ for reaction kinetics, the same problems will be present whether one uses "activity" or any other concept in their development. The separation of the temperature dependence of the physical movement from $f(\alpha)$ and uniting it with the temperature dependence of the chemical reaction, $k(T)$, will not change the final form of a properly formulated rate expression. However, the concept of activity of the reacting species gives a more vivid picture of what is going on and may be a psychological help in arriving at this proper formulation.

In this paper, we have tried to stress the roll of $f(\alpha)$ in the temperature dependence of the rate and how this temperature dependence can have forms other than the Arrhenius equation such as the WLF equation or step functions. The importance of the concept of "rate controlling step" in the simplification of the rate equation was emphasized and the significance of the compensation effect was discussed.

It was found to be necessary to have temperature and rate data which cover a wide range of values to test the applicability of the Arrhenius equation. It is satisfying when one obtains a good fit of the data over the whole of such an extended temperature range. However obtaining a constant E does not prove that one has a correct model for the kinetics mechanism. To answer the question, "How does one know if one has the correct form of $f(\alpha)$?", each proposed equation must be tested under many differing experimental conditions systematically to see how its parameters change with temperature, heating rate, specimen weight, geometry, degree of subdivision and thermal pretreatment, purge gas conditions, and all other procedural factors which might affect the rate. Maciejewski [21] has published recently an excellent and provocative discussion of many of the problems which we must face when we try to interpret solid state kinetics. Thermal analysis is capable of giving only a part of the information needed for assigning reaction mechanism. Other techniques which determine the chemical and physical changes even more directly should be employed concurrently with thermal analysis methods. Examples of such techniques are Fourier transform infrared spectroscopy, gas chromatography, mass spectrometry, X-ray, electron and neutron diffraction, various microscopic techniques, etc.

This paper has not presented any great breakthrough in modeling thermal analysis kinetics. However, it is hoped that it has brought in focus a few old concepts that one may lose sight of when becoming bogged down with the fine structure of modeling the kinetics of a specific reaction system.

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Zusammenfassung — Bei der Modellierung der Temperaturabhängigkeit der Kinetik bei heterogenen, kondensierten Phasen treten spezielle Probleme auf. In der Unterteilung des Modelles für die Reaktionsgeschwindigkeit in zwei Teile: a) $f(\alpha)$ ist physikalisch (Translation) und b) $k(T)$ ist chemisch (Vibration) treten bei der Definierung der Temperaturabhängigkeit von Teil a) und dann bei der Verknüpfung mit der Arrhenius-schen Temperaturabhängigkeit von Teil b) Komplikationen auf. Es wird die Rolle von $f(\alpha)$ in thermoanalytischen Systemen besprochen. An einer Vereinfachung des temperaturabhängigen Termes wurde das Konzept des geschwindigkeitsbestimmenden Schrittes angewendet. Es wird die Bedeutsamkeit des Kompensationseffektes in diesen Systemen beschrieben und dafür eine heuristische Vereinfachung vorgeschlagen. Praktisch gesehen maximale Temperaturbereiche für thermoanalytische Experimente sowie der Einfluß der Ungenauigkeit der Temperaturmessung für die erhaltenen Arrhenius-Parameter wird diskutiert. Die zur Beschreibung der Temperaturabhängigkeit von $f(\alpha)$ benutzten WLF und anderen Gleichungen stellen keine Kompatibilität mit der Arrhenius-schen Gleichung her.