Journal of Thermal Analysis, Vol. 49 (1997) 17-32

STEPS IN A MINEFIELD
Some kinetic aspects of thermal analysis

M. E. Brown

Chemistry Department, Rhodes University, Grahamstown, 6140 South Africa

Abstract

This paper is a review of some of the controversial kinetic aspects of thermal analysis, starting from the 'Šesták questions' posed in 1979 and looking at developments in some areas since that time. Aspects considered include: temperature programmes and variations, models and mechanisms, kinetic parameters, distinguishability and extent of fit of kinetic models, complementary evidence for kinetic models, the Arrhenius equation and the compensation effect. The value of the ideas of non-isothermal kinetics in chemical education is emphasized.

Keywords: Arrhenius equation, compensation, distinguishability, kinetics, mechanisms, non-isothermal

Introduction

When one attempts to read the intimidating and rather indigestible literature of kinetics of solid state processes and, in particular, the papers on non-isothermal kinetics (NIK), one cannot help noticing the similarities between Science and Religion. Those who believe that they have found the 'true way' promote their points-of-view with evangelistic fervour and often mention with contempt, or even attack, the practices of the 'heathen'. The field is full of dogma: 'Thou shalt do this.....and thou shalt not do the other'! An agnostic in the field (defined as a person who is uncertain or noncommital) searches, perhaps in vain, for what is useful and what is not.

An interesting book [1] on kinetics, 'The Interpretation and Use of Rate Data: the Rate Concept', by Stuart W. Churchill, who was at that time a Professor of Chemical Engineering at the University of Pennsylvania, has a wonderful collection of quotations, from a wide variety of sources, many of which apply very aptly to our turbulent area. For instance:

'False facts are highly injurious to the progress of science for they often endure long; but false views if supported by some evidence, do little harm for everyone takes a salutary pleasure in proving their falseness.' Darwin and: 'Everybody calls 'clear' those ideas which have the same degree of confusion as his own.' Proust.

Šesták's questions

In 1979, J. Šesták, recipient of the Mettler Award in 1974 and who has made numerous important contributions to both the philosophy and the practice of the subject, pub-

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

lished [2] a series of thought-provoking questions on the subject (Table 1) and his responses to the questions at that time [2]. Many of these questions are still unresolved.

Table 1 The Šesták questions [2]

(1) Q: Why has non-isothermal kinetics gained so bad a reputation? Is it due to experiments carried out mainly by thermoanalysts?

(2) Q: Non-isothermal kinetics, in fact, is liable to pay for the mode of its historical introductions. Where are the roots of possible misfits and where can we best learn the basis of non-isothermal treatments?

(3) Q: What do kinetic parameters such as activation energy and reaction-order really mean? Are these terms generally applicable, particularly assuming solid-state processes?

(4) Q: some authors advocate either the separability or non-constancy of kinetic data. Is this true, and how is it related to the so-called kinetic compensation effect?

(5) Q: Which method of kinetic data evaluation is better, differential or integral?. (quite a common question!).

(6) Q: What about the accuracy of kinetic data calculation? Is this only a consequence of the accuracy of the experimental input data, or can it be further affected by its mathematical treatment?

(7) Q: There are controversial views regarding the reliability of the most popular TA method, DTA. Is it useful for kinetic studies or is it too dependent on its experimental set-up and thus more suitable for analytical applications only?

(8) Q: If there are so many troubles with the gradients, would it be better to employ only isothermal methods? What, in fact, is the difference between iso and non-iso-data?

(9) Q: Can we ever speak about thermodynamics in terms of dynamic thermal experimentation, how compatible are kinetic and equilibrium data; and what then is the equilibrium background of the process?

(10) Q: The year 1970 was full of activity in seeking the fundamentals of correct representation of the non-isothermal kinetic equation, which was initiated by MacCallum and Tanner's article. What in fact is the essence of this problem?

(11) Q: Is it worth paying such attention to non-isothermal kinetics? Is it merely good for a narrow region of interested scientists, and how about the already-mentioned publication policy?

(12) Q: The offensive of computing techniques in all branches of science and engineering has not certainly avoided the field of TA. Will computers be of real help in our kinetic work, or will they solve only the most painful numerical troubles?

Flynn's stages

Professor J. H. Flynn, recipient of the Mettler Award in 1980 and Chairman of the ICTAC Kinetics Committee since its inception, has published widely [3 and references therein] on theoretical aspects of kinetics and on an important practical aspect of kinetic studies, namely the prediction of lifetimes of materials, particularly polymers. He recalls [4] an analogy which he used in which he compared the stages of coping with chronic pain by a sufferer, with the manner in which one copes with the extraction of kinetic information from studies of reactions of solids. These stages are: (i) hopeful euphoria; (ii) periods of frustration and despair; and finally (iii) low expectation.

Garn's warnings

Another very influential figure in the field, Professor Paul D. Garn, published a set of 'cautions' [5] in 1972 which could well be supplied by manufacturers to purchasers of TA equipment.

In summary, these included warnings to researchers to consider carefully factors such as:

- the history of pre-treatment of the sample;
- the reversibility of reaction and diffusive removal of gaseous products;
- surface and particle size effects;
- self-heating, self-cooling and heat transfer;
- the approximate nature of kinetic models, and
- the uncritical application of the Arrhenius equation.

Other points of view

Boldyreva [6] states that the only argument in favour of NIK studies is their rapidity compared with isothermal studies. In certain technological situations, e.g. processes carried out under non-isothermal conditions, the rapidity of the information and the experimental similarities to process conditions 'may compensate for the absence of a physical meaning'. She also criticizes the use of NIK studies for the determination of kinetic mechanisms in the absence of more direct studies.

Maciejewski [7] questions the usefulness of kinetic data for solid state reactions, under the title 'Somewhere between fiction and reality'. He rightly warns of the dangers of regarding measured kinetic parameters as characteristic of the sample, without reference to the experimental conditions used.

Temperature programmes and variations

A major source of tension in kinetic studies using TA is the division between those who promote experimentation under isothermal conditions and those who believe that the 'true way' is via programmed (linear rising) temperature experiments. Criado *et al.* [8] have pointed out that the alternative types of experimental conditions are both approximations to the true sample temperature.

Fortunately these two major 'parties' are being diluted (or infiltrated?) by supporters of other possibilities, e.g., constant rate thermal analysis, CRTA (Rouquerol and Reading [9]), modified further by Criado *et al.* [10] to constant acceleration TA; temperature jump methods (Sorensen and others [11]); and, more recently, modulated temperature programmes (Reading [12], Wunderlich [13] and others). On the fringes of these groups, possibly watching with some amusement, are those who work with energetic materials, like explosives or pyrotechnics, who have long struggled with the problem of determining kinetic parameters of reactions which occur under temperature conditions determined by the heat release during reaction and the heat transfer properties of the reaction system and its surroundings (Boddington and Laye, see reference [14] and literature cited). This last situation has been tackled very successfully by the Leeds group [14] who used the relatively simple experimental technique of measuring the profile of temperature rise against time as the self-propagating combustion front passes a fine thermocouple inserted in a pressed column of pyrotechnic mixture. The interesting question arises as to whether the definition of thermal analysis would exclude such a fundamental measurement? The temperature rise is 'programmed' by the reaction itself? As always, the results of simple measurements require sophisticated mathematical treatment to extract the maximum amount of information. A typical temperature profile obtained for combustion of a 30% Sb/$KMnO_4$ pyrotechnic composition [15] is shown in Fig. 1. To extract the kinetic parameters for the reaction concerned requires [14] resolution of the various thermal power contributions. To do so usually involves using a reaction order (*RO*) type of rate equation, but acceleratory models show promise of providing a better description of the combustion [16]. An interesting application of this theory to more conventional thermal analysis is the finite-element modelling of the combustion of a sample of pyrotechnic composition in the sample holder of a conventional DTA instrument [17, 18].

Arguments on the relative value of non-isothermal and isothermal methods of kinetic analysis are generally unproductive. The results of some kinetic studies using non-isothermal techniques are in good agreement with those obtained on the same system using isothermal methods. By contrast, other systems are reported to give kinetic results which are very dependent on the technique used. Thus the complementary use of the two approaches can be valuable in revealing potential sources of difference, such as those discussed above. Both techniques can provide valuable insights into the processes occurring, provided that the experimenter is critically aware of the shortcomings and limitations of both approaches.

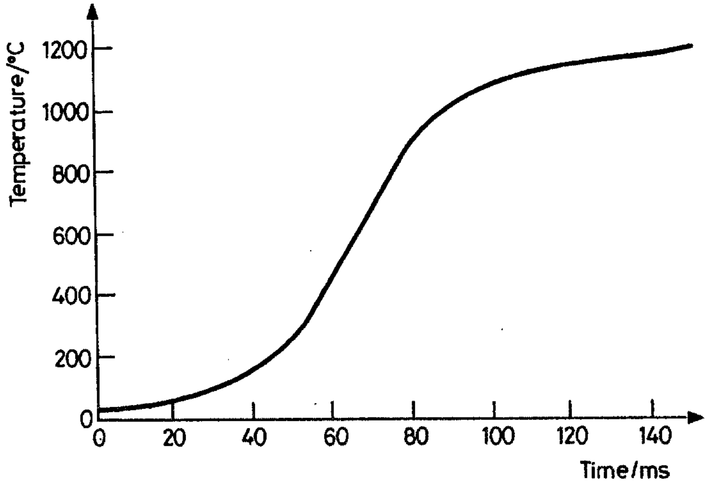


Fig. 1 A typical temperature-time profile for the combustion of a 30% Sb/$KMnO_4$ pyrotechnic composition [15]

Mechanisms and models

In the literature, there is considerable ambiguity in the use of the term reaction mechanism. Sometimes it has the meaning, common to homogeneous kinetics, of describing the chemical steps by which reactants are converted to products. Often, however, the term is used to describe the rate equation and, by implication, the geometrical or other model on which the rate equation is based. In homogeneous kinetics, one would not imply that the fact that the experimental data could be described by, for example, a second-order rate equation revealed much about the mechanism other than the possibility of control by a bimolecular reaction step. The chemical nature of such a step would be referred to as the reaction mechanism. In solid state reactions, information on the chemical steps involved can be very difficult to obtain and many kinetic studies do not proceed beyond identification of the most appropriate rate equation (or kinetic model) from a rather limited selection.

The above identification procedure is also a source of controversy. There are those who go to considerable effort to avoid the identification procedure through use of methods labelled as 'non-discriminatory' or, more neutrally, as 'isoconversional' [19, 20], while others [2] regard the identification of the rate equation as the prime object of kinetic studies.

Kinetic parameters

Whether rate measurements from a single experiment extending across a range of temperatures are, in principle, capable of providing a complete kinetic analysis (the form of $f(\alpha)$ or $g(\alpha)$ and the magnitudes of E_a and A) has been debated. Agrawal [21] discussed some of the problems of the uniqueness of the derived parameters. Problems occur whenever attempts are made to estimate more than two parameters from a single curve. Use of kinetic expressions containing multiple α terms also leads to non-unique kinetic parameters, as does the existence of an apparent compensation effect. Criado *et al.* [8] have shown that a single TG curve can be generated using three different kinetic models with different Arrhenius parameters.

Málek [22] has given an excellent account of the correlation between kinetic parameters and the kinetic models from which they are derived. As a consequence of the correlation between E_a and A (the so-called 'compensation effect') a TA curve can be described by a model and an associated apparent E_a value, instead of the true model and true E_a value, where

$$(E_a)_{\mathrm{app}} = F(E_a)_{\mathrm{true}}$$

and the multiplying factor, F, is characteristic of the true kinetic model. Values of such factors are given.

Vyazovkin and Lesnikovich [19] point out that the kinetic parameters calculated from isothermal data are not very dependent upon the kinetic model chosen, while the opposite is true for non-isothermal methods. They suggest that this is a reason for determining the kinetic parameters from isothermal measurements and the kinetic model from non-isothermal measurements.

The reported lack of agreement amongst kinetic parameters calculated from the same set of experimental data using different mathematical analyses [23, 24] is disturbing. Some of the commercially available programs for kinetic analysis do not even specify the algorithms on which they are based, while other packages base analyses on kinetic expressions restricted to the reaction order (*RO*) type.

Vyazovkin and Lesnikovich [19] emphasize the need for careful statistical testing of the significance of the calculated parameters. Such tests may, at least, decrease the number of kinetic models which need to be considered. They specifically warn against the practice of forcing the model to be of the reaction order (*RO*) type where the value of n may not be interpretable. Coincidence of the parameters calculated by various different methods confirms only the equivalence of the methods of calculation and not the validity of the parameters obtained.

One of the arguments against the use of 'discrimination' methods [19] is that the set of models from which the 'best model' is to be chosen is too limited. Hence one of the set is going to be the 'best model' even if the set does not contain the true model. The formal models in the elementary set (e.g., [23]) are too simple to account for all the features of real processes. Modification of the models, however, results in an increased number of adjustable parameters.

Vyazovkin and Lesnikovich [25] have discussed the possible solving of the IKP using methods based on generalized descriptions, (or 'synthesis' rather than 'analysis'). These methods are based upon the premise that different aspects of the real process may be best described by a synthesis of individual features of competing ideal models. Such a generalized description is the Šesták-Berggren approach using

$$f(\alpha) = \alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}$$

which, depending on the exponents, may represent the usual set of models. The number of parameters which can be determined depends upon the experimental data [21, 22]. Usually a maximum of two of the three exponents can be determined.

Wyandt and Flanagan [26] describe the use of the Šesták-Berggren equation in a nonisothermal kinetic method suggested by Zimmerman [27]. The logarithmic form of the kinetic equation

$$d\alpha/dT = (A/\beta)\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}\exp(-E_a/RT)$$

is

$$\ln(d\alpha/dT) = \ln(A/\beta) + m\ln(\alpha) + n\ln(1-\alpha) + p\ln[-\ln(1-\alpha)] + (-E_a/RT)$$

This expression can be used in matrix form in order to make it amenable to solution as a system of linear equations [26]. Eight data sets (α, $d\alpha/dT$, T) are collected for each TG run. The matrices are then solved and values for m, n, p and E_a are determined. No assumptions are made about the mechanism of the solid-state process being investigated. Values for m, n and p are calculated directly from the data. Once values are known, the most likely mechanistic model can be selected.

Generalized descriptions include restriction to a class of model (e.g., reaction order or Avrami-Erofeev), i.e. using only one of the terms in the above equation, but placing no restriction on the value of the exponent. Also suggested are linear combinations of several formal models. Vyazovkin and Lesnikovich [25] have shown that the Avrami-Erofeev model is equivalent to linear combinations of some of the other formal models and hence may serve as a generalized description. Generalized descriptions may also include approximating functions, such as polynomials, splines, etc., but the number of adjustable parameters becomes unwieldy and the parameters lose both their independence and their physical significance.

Again, some quotations from Churchill's book [1] are appropriate:

'No satisfactory justification has ever been given for connecting in any wav the consequences of mathematical reasoning with the physical world.' E. T. Bell 'Mathematics is the only science where one never knows what one is talking about nor whether what is said is true.' Bertrand Russell.

Distinguishability

In 1979, Brown and Galwey [28] published a paper on the distinguishability of kinetic models under isothermal conditions. This paper has been well cited over the years. Figure 2 shows the close resemblance of the contracting-area (R2) and contracting-volume (R3) models, and Fig. 3 a similar difficulty of distinguishing the Avrami-Erofeev models (A3 and A4) under isothermal conditions. All four curves are based on the same Arrhenius parameters ($A=1.88\times10^{15}$ min^{-1}, $E_a=$ 100 kJ mol^{-1}).

When linearity of plots of $g(\alpha)$ against time was examined [28], correlation coefficients, r, of 0.9979 were obtained for incorrect analyses of R2 data in terms of the R3 model and vice versa. Deviations from linearity were greatest in the mid-alpha range. Correlation coefficients were even higher (0.9989) for incorrect analyses of the A3/A4 combination. The A3 and A4 models are also extremely difficult to distinguish from the Prout-Tompkins (B1) model [28].

More recently [29] plots of isothermal rate data against model data were examined. This method was more successful in distinguishing the A3 and A4 models than it was for the R2 and R3 models. Other approaches tried were plots of ratios of rates (experiment/model) against alpha, and plots of ln(experimental rate) against ln(model rate), both of which approaches showed promise for distinguishing diffusion models (D1 to D4) [29].

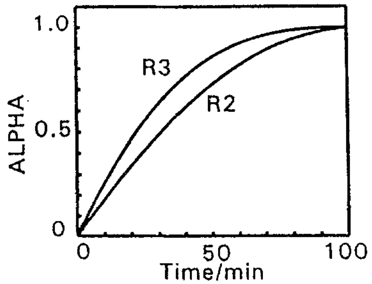


Fig. 2 Distinguishability of the contracting area (R2) and contracting volume (R3) models under isothermal (302 K) conditions. $E_a=100$ kJ mol^{-1}, $A=1.88\times10^{15}$ min^{-1}

Because of such difficulties under isothermal conditions, it could be expected that analysis of programmed temperature data would be even more difficult. Alpha-temperature curves at a linear heating rate, $\beta=1$ K min^{-1}, are shown in Figs 4 and 5, respectively.

In an extremely valuable paper, Criado, Ortega and Gotor [8] point out that by adjustment of the Arrhenius parameters, several kinetic models of widely different types (F1, A2 and D3 in their example) can give identical alpha-temperature curves.

Using constant rate thermal analysis (CRTA) [9], the resulting temperature-time plots (constant rate = 1.0 min^{-1}) are shown in Figs 6 and 7, respectively.

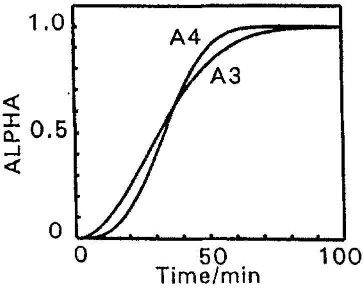


Fig. 3 Distinguishability of the Avrami-Erofeev (A3) and (A4) models under isothermal (310 K) conditions. $E_a=100$ kJ mol^{-1}, $A=1.88\times10^{15}$ min^{-1}

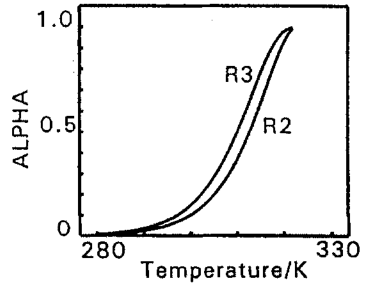


Fig. 4 Distinguishability of the contracting area (R2) and contracting volume (R3) models under programmed temperature (1.0 K min^{-1}) conditions. $E_a=100$ kJ mol^{-1}, $A=1.88\times10^{15}$ min^{-1}

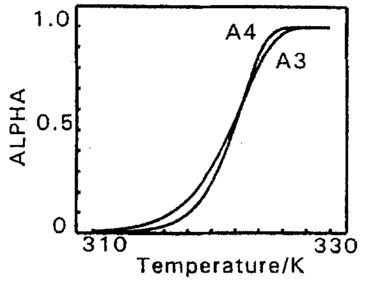


Fig. 5 Distinguishability of the Avrami-Erofeev (A3) and (A4) models under programmed temperature (1.0 K min^{-1}) conditions. $E_a=100$ kJ mol^{-1}; $A=1.88\times10^{15}$ min^{-1}

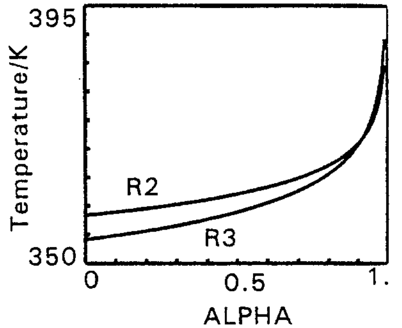


Fig. 6 Distinguishability of the contracting area (R2) and contracting volume (R3) models under constant rate (1.0 min^{-1}) conditions. E_a = 100 kJ mol^{-1}; A = 1.88x10^{15} min^{-1}

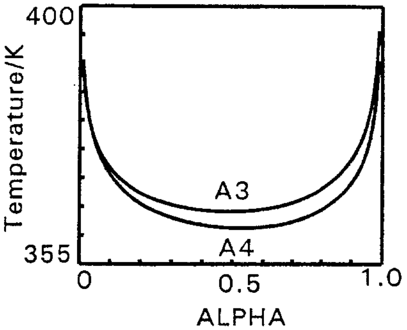


Fig. 7 Distinguishability of the Avrami-Erofeev (A3) and (A4) models under constant rate (1.0 min^{-1}) conditions. E_a = 100 kJ mol^{-1}, A = 1.88x10^{15} min^{-1}

Extent of fit

There is also a more minor division between those workers who choose to describe their experimental results in terms of partial application of various models over different regions of time or temperature, and those who prefer to describe their results in terms of approximate agreement with a single model (or very limited number of models) over as wide a range of α as possible, allowing for deviations from ideality arising from factors such as variations in particle size and shape. As mentioned above, the ideal is to introduce as few adjustable parameters as possible.

Complementary evidence

Galwey has given numerous powerful examples of the use of electron microscopic examination of the surfaces of decomposing solids in support of proposed kinetic models [30]. He has also used various methods of wet-chemical analysis, including NMR, to formulate reaction mechanisms. Even these advances have to be balanced against the caution of esták [31] who pointed out some of the dangers of attempting to correlate the results of the averaged measurements produced by TA methods with microscopic detail of a very limited portion, i.e. the surface, of the sample which may even be susceptible to damage during the investigation, e.g., by the electron beam in SEM.

X-ray diffraction studies using synchrotron radiation have aroused considerable excitement in the detailed information available [32], but how many researchers have access to such facilities?

The Arrhenius equation

This inoffensive, relatively simple and originally empirical relationship has become a surprising source of heated (!) debate. It has even been disparagingly referred to as the 'erroneous equation'. The most informative papers by Laidler [33, 34] have, unfortunately, not received the attention which they richly deserve. In one of these papers [33], Laidler describes the variety of phenomena which have been found to follow an Arrhenius-type of temperature dependence. Examples are listed in Table 2. These entertaining examples were used [28] to stress:

(i) the possibility that complex processes can show an Arrhenius temperature dependence; and

(ii) the apparent control of many phenomena by chemical processes.

The most precise application of the Arrhenius equation to processes involving solids has been in the diffusion of ions [35, 36] and in numerous studies of the diffusion of crystal imperfections. Defects are often major participants in reactions of solids.

In another key paper [34], Laidler discusses the alternatives to the Arrhenius equation. He shows that the temperature ranges over which most experimental data are obtained are so limited that many alternative plots, e.g.,

- $\ln k$ *vs.* T; or
- $\ln k$ *vs.* $\ln T$ (Harcourt and Esson [37]), cannot be distinguished from the conventional Arrhenius plot of
- $\ln k$ *vs.* $1/T$, because plots of T *vs.* $1/T$, or *vs.* $\ln T$ are approximately linear over a limited T interval.

Table 2 Unconventional applications of the Arrhenius equation [33]

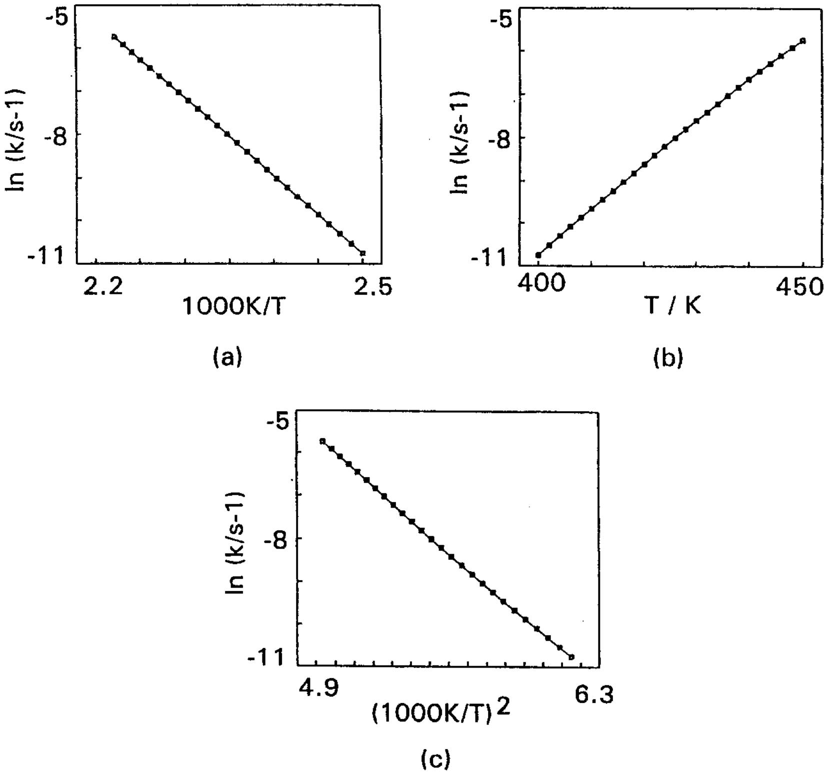
Phenomenon	E_a/kJ mol^{-1}
Chirping of tree crickets	51
Creeping of ants	51
Flashing of fireflies	51
Terrapin's heart beat	77
Alpha brain wave rhythm	29
Rate of counting	100
Rate of forgetting	100

Galwey and Brown [38] have calculated a set of k–T values at 2 K intervals between 400 and 450 K for a reaction with the Arrhenius parameters:

$$\ln (k/\mathrm{s}^{-1}) = 34.351 - 150\,000/RT$$

These values were selected as being typical of a kinetic investigation of a solid state reaction. Reaction is completed in 500 s (8.3 min) at 450 K, which is about the minimum reaction time to avoid effects of self-heating or self-cooling. Experiments at 400 K would be completed in about 22 h. Plots of $\ln k$ *vs.* $(T/\mathrm{K})^{-1}$ are exactly linear (Fig. 8(a)), but plots of $\ln k$ *vs.* (T/K) (Fig. 8(b)) are also close to linear ($r^2=0.9990$ and the standard error of the slope was <1%). A plot of $\ln k$ *vs.* $(T/\mathrm{K})^{-2}$ for the same data (Fig. 8(c)) shows deviations that are even smaller ($r^2=0.9997$ and the standard error of the slope was 0.3%). Plots of k *vs.* $(T/\mathrm{K})^n$ were linear only when $n>16$, and no physical significance has been given to the value of n.

Benson [39] has calculated that to measure k to ±1%, T must be known to 0.03%. Temperature control to ±1 K at about 600 K leads to uncertainties in k of about ±5% and about ±10% in E_a. Significant deviations from linearity of data would thus not be detected in plots of $\ln k$ *vs.* $(T/\mathrm{K})^{-2}$, $(T/\mathrm{K})^{-1}$ or T/K from data collected in most kinetic investigations.



(a)

(b)

(c)

Fig. 8 The Arrhenius plot ($\ln k$ *vs.* $1/T$) (a); $\ln k$ *vs.* T (b); and $\ln k$ *vs.* $1/T^2$ (c)

Significance of the Arrhenius parameters

This has also been a widely debated subject. Most reactions involving solids take place at interfaces of some sort. At the interface, there is necessarily a change of solid-state band structure. The band structures for the transition between *p* and *n* zones of a semiconductor are the consequences of small changes in impurity concentrations within a dominant regular crystal structure. In the representation of band structures, single site vacancies or impurity sites are represented by localized electron-accommodating levels at energy values different from those of the band levels of the host crystals. Chemical species, situated at the interface in a locally modified bonding environment during reaction, can similarly be expected [38] to be associated with a band structure containing levels (interface levels) that differ from those of the reactant and of the product, see Fig. 9.

The band structure across the reaction zone may be heavily distorted (dotted lines in Fig. 9) or even absent. The processes essential for reaction (electron transfers or bond redistributions) occur within this zone. These interface levels, capable of accommodating electrons, represent the precursor energy states to the bond redistribution step and account for the increased reactivity relative to similar components in more perfect crystalline regions. Occupancy of these levels can be described by an energy distribution function similar in form to the Maxwell-Boltzmann distribution function which provides the starting point for a theoretical explanation of Arrhenius behaviour in homogeneous reactions. Although the Max-

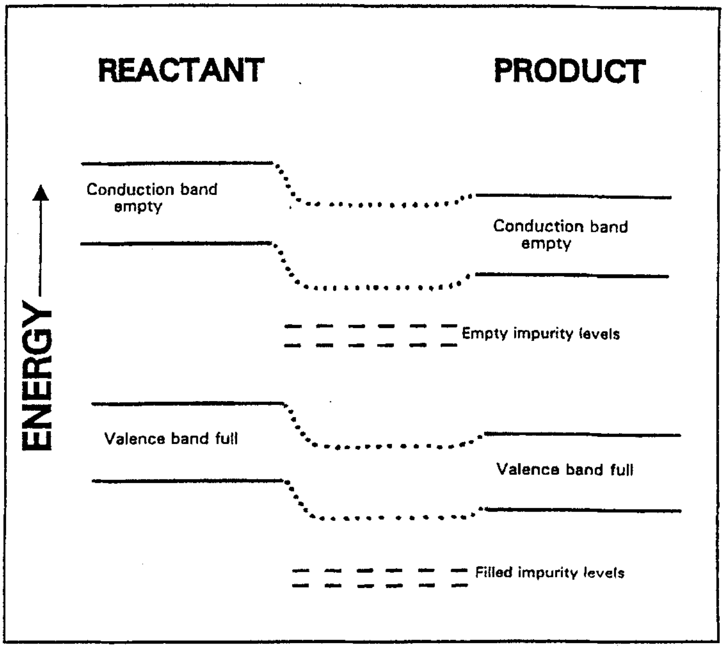


Fig. 9 Electron energy levels at the reactant-product interface [33]

well-Boltzmann model is inapplicable to the immobilized constituents of a solid, energy distributions of similar form arise amongst the most energetic quanta. For values significantly above the Fermi level, both electronic energy (Fermi-Dirac statistics) and phonon energy (Bose-Einstein statistics) distributions approximate [38] to the same form as that in the Maxwell-Boltzmann distribution and hence are capable of explaining the fit of k–T data to an Arrhenius-type equation.

Even if all physical explanations are rejected, the Arrhenius parameters, which are procedurally clearly defined, serve a useful empirical purpose for comparing temperature dependences of reactions, e.g., in hazard evaluation, and in attempts to predict behaviour at interpolated (or, with great caution, extrapolated) temperatures [3].

Much has been made of the wide range of values of E_a and A for decomposition of a single substance, e.g., calcium carbonate, obtained under a variety of conditions [40]. This shows that the 'apparent' Arrhenius parameters are not simple constants, but complex parameters containing factors related to the reaction conditions. Instead of discarding such information as useless, surely the challenge is to identify these factors by careful study?

The compensation effect

A 'compensation-type' of relationship between Arrhenius parameters

$$\ln A = bE_a + c$$

has been associated with two (totally different?) groups of reactions:

(i) Reactions of a series of similar compounds (assuming 'real' Arrhenius parameters), and

(ii) Behaviour of a single compound under different experimental conditions (hence 'apparent' Arrhenius parameters).

Since there is argument whether the relationship is 'real' or 'apparent', and little agreement on the interpretation of the constants b and c, I personally find the notion of an 'apparent' relationship between 'apparent' parameters, unattractive. No one has yet claimed a compensation relationship for the results of kinetic analyses of one set of input data by different mathematical procedures!

Education

Exposure of higher-level students to the ideas of non-isothermal kinetics is valuable [41]. So much emphasis is placed on isothermal experimentation in standard kinetic treatments, that it is a definite 'mind-broadening' jump to consider the possibility of obtaining kinetic information from programmed temperature experiments. When such ideas are coupled with the special features of the kinetics of the reactions of solids [23] (where terms such as 'concentration' have to be adapted, and mobility of and contact between reactants become important factors compared to homogeneous reactions) the educational value increases further.

Conclusions

I should like to end with three quotations which put things better than I could hope to. Ninan [42] concludes: 'There is an everlasting controversy between isothermal and non-isothermal and between mechanistic and non-mechanistic approaches...each has its own merits and drawbacks. The mechanism of a thermal decomposition reaction cannot be assigned unequivocally from the mathematical curve fitting of the TG data alone, whereas the isothermal mass-loss data give a better insight into the reaction mechanism. As far as the values of the kinetic parameters are concerned, there is no significant difference between isothermal and non-isothermal methods or between mechanistic and non-mechanistic approaches, in the sense that they show the same degree of fluctuation or trend, as the case may be. Thus, for the purpose of calculating the kinetic constants, the non-isothermal method has the advantage of greater simplicity. However, one has to ascertain the influence of procedural factors on the kinetic parameters before making any conclusion regarding the kinetics and mechanism of a solid state thermal decomposition reaction. Finally, it may be possible to superimpose the effects of the individual procedural factors, in order to predict the kinetic parameters for any set of experimental parameters.'

Once more from Churchill's inspiring book [1]: 'Our ability and inclination to postulate and construct models appear to exceed our ability and inclination to obtain good rate data. Improvement in rate correlations will come primarily from more and better measurements rather than from improvements in modeling or mathematical procedures.'

'Scientists have odious manners, except when you prop up their theory; then you can borrow money of them.' Mark Twain.

* * *

On an occasion such as this, I should like to acknowledge the early inspiration and training of Professor E. G. Prout; the encouragement and help of Professor Leslie Glasser in acquiring our first thermal analysis equipment; the friendship of, and many fruitful years of collaboration with Dr. Andrew Galwey, who has made many contributions to the topic of this lecture; and Professor Patrick K. Gallagher for so much encouragement, interest and support. I am also deeply grateful to Mettler for sponsoring this award and to NATAS for administering it.

References

1 S. W. Churchill, The Interpretation and Use of Rate Data: The Rate Concept, McGraw-Hill, New York, 1974, p. 317–319.
2 J. Šesták, J. Thermal Anal., 16 (1979) 503.
3 J. H. Flynn, J. Thermal Anal., 44 (1995) 499.
4 J. H. Flynn, personal communication, 1996.
5 P. D. Garn, Crit. Rev. Anal. Chem., 3 (1972) 65.
6 E. V. Boldyreva, Thermochim. Acta, 110 (1987) 107.
7 M. Maciejewski, J. Thermal Anal., 38 (1992) 51.
8 J. M. Criado, A. Ortega and F. Gotor, Thermochim. Acta, 157 (1990) 171.
9 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal., 29 (1984) 775.

10 A. Ortega, L. A. Pérez-Maqueda and J. M. Criado, Thermochim. Acta, 239 (1994) 171; J. Thermal Anal., 42 (1994) 551.

11 O. Toft Sørensen, Thermochim. Acta, 50 (1981) 163.

12 P. S. Gill, R. Sauerbrunn and M. Reading, J. Thermal Anal., 40 (1993) 931.

13 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.

14 P. G. Laye, Phil. Trans. R. Soc. Lond. A, 339 (1992) 387.

15 M. W. Beck and M. E. Brown, Pyrotechnics, Proceedings of the 10th International Pyrotechnics Seminar, Fraunhofer-Institut für Treib- und Explosivstoffe, Karlsruhe, 1985, paper 14.

16 S. J. Taylor and M. E. Brown, to be published.

17 M. W. Beck and M. E. Brown, JCS Faraday Trans., 87 (1991) 711.

18 M. W. Beck and M. E. Brown, Thermochim. Acta, 164 (1990) 379.

19 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 35 (1989) 2169.

20 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 36 (1990) 599.

21 R. K. Agrawal, Thermochim. Acta, 203 (1992) 93.

22 J. Málek, Thermochim. Acta, 200 (1992) 257.

23 M. E. Brown, D. Dollimore and A. K. Galwey, Comprehensive Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.

24 J. Málek and J. M. Criado, Thermochim. Acta, 175 (1991) 305.

25 S. V. Vyazovkin and A. I. Lesnikovich, Thermochim. Acta, 122 (1987) 413.

26 C. M. Wyandt and D. R. Flanagan, Thermochim. Acta, 197 (1992) 239.

27 J. Zimmerman, MS Thesis, Illinois State University, Normal, Illinois, USA, 1983.

28 M. E. Brown and A. K. Galwey, Thermochim. Acta, 29 (1979) 129.

29 A. K. Galwey and M. E. Brown, Thermochim. Acta, 269/270 (1995) 1.

30 M. E. Brown, A. K. Galwey and G. G. T. Guarini, J. Thermal Anal., 48 (1997)

31 J. Šesták, J. Thermal Anal., 36 (1990) 1997.

32 V. V. Boldyrev, Y. A. Gaponov, N. Z. Lyakov, A. A. Politov, B. P. Tolochko, T. P. Shakhtshneider and M. A. Sheromov, Nucl. Inst. Methods Phys. Res., A261 (1987) 192.

33 K. J. Laidler, J. Chem. Educ., 49 (1972) 343.

34 K. J. Laidler, J. Chem. Educ., 61 (1984) 494.

35 J. Corish and P. W. M. Jacobs, J. Phys. Chem. Solids, 33 (1972) 1799.

36 P. W. M. Jacobs, J. Corish and C. R. A. Catlow, J. Phys. C, 12 (1979) 3433; 13 (1980) 1977.

37 A. V. Harcourt and W. Esson, Proc. R. Soc. Lond., A 14 (1965) 470.

38 A. K. Galwey and M. E. Brown, Proc. R. Soc. Lond., A 450 (1995) 501.

39 S. W. Benson,The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960, p. 91.

40 J. Zsakó and H. E. Arz, J. Thermal Anal., 8 (1974) 651.

41 M. E. Brown and C. A. R Phillpotts, J. Chem. Educ., 55 (1978) 556.

42 K. N. Ninan, J. Thermal Anal., 35 (1989) 1267.

Presentation of NATAS-Mettler Award. The recipient was Professor Michael E. Brown. The award was presented by Mr. Tom Basalik of Mettler-Toledo. Congratulations!