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HAZARD EVALUATION BY THERMAL ANALYSIS

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This report describes briefly the most frequently cited 'named' methods for kinetic analysis by thermoanalytical methods. Some were developed for thermogravimetry (TG) and differential thermal analysis (DTA) but the concern here is only with their application to differential scanning calorimetry (DSC), a technique commonly employed by HSE's Health & Safety Laboratory at Buxton in investigating the exothermicities and decomposition kinetics of energetic materials. Twenty-six key references are cited.

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Hazard Evaluation by Thermal Analysis

Health and Safety Executive

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Department of Physical Chemistry, The University, Leeds LS2 9JT

The research contract has been concerned mainly with the use of differential scanning calorimetry (DSC) to obtain kinetic parameters. This report complements the account already given in ref. (1). Thermal analysis has considerable scope in hazard evaluation but the interpretation of experimental results is not straightforward. Further, the relevance of the information gained is not self-evident bearing in mind the very small scale of the experiments and the use of specially prepared samples. The determination of onset temperatures depends on the sensitivity of the equipment with scanning microcalorimetry offering a possible increase in resolution. Exothermicity values, at best usually ill-defined quantities, may depend on sample size and containment. The use of thermal analysis to investigate reaction kinetics is a contentious issue with some authors claiming that it is virtually impossible to obtain useful information. They point out that merely changing the design of the crucible may be sufficient to affect significantly the shape of the thermal analysis curve. The present consensus of opinion is that there is a valid basis for the investigation of kinetics. Even so the interpretation of the results is often naive. The literature abounds with kinetic results quoted to an absurd number of significant figures with no consideration of the experimental errors.

A number of analytical procedures have been proposed which offer a quick route to the kinetic parameters. It is rational for the Health and Safety Laboratories to use these in view of the limited time at their disposal. Such procedures involve assumptions often

not stated explicitly, e.g. the absence of thermal lags and temperature gradients in the sample. Other assumptions deal specifically with the kinetic schemes. These are based on separable kinetics, i.e. $da/dt = f(\alpha)g(T)$, in which the temperature dependence is expressed by an Arrhenius term, $g(T) = AT^P \exp(-E/RT)$. The dependence on the extent of reaction α is often assumed to be n th order, $f(\alpha) = (1-\alpha)^n$ or even first order although such a simplistic approach is most unlikely to represent the behaviour of solid-state reactions. Alternative approaches have been discussed by Sestak and Berggren (2) but in practise the shape of thermal analysis curves is not very sensitive to the form of the isothermal law.

We have investigated the use of a representative number of analytical procedures for isothermal and dynamic experiments. A major problem associated with the dynamic experiments is the assignment of the base line which influences both the rate and extent of reaction derived from the thermal analysis curve. We have used the conventional 'straight-line' construction but recognise that it gives rise to uncertainty in the kinetic results. The derivation of a more realistic base line requires further experimental effort. The aim is to determine the relevant heat capacities but this is not always possible because of the complicated curve shapes. The absence of heat capacities also precludes the use of alternative thermodynamic approaches to the kinetic analysis.

The ASTM test method E 698, 'Arrhenius Kinetic Constants for Thermally Unstable Materials', incorporates the analyses proposed by Ozawa (3) and Kissinger (4). It considerably extends the earlier test method E 537 which was concerned with the detection of energy changes. The experiments are dynamic and easier to carry out than those under isothermal conditions. The procedure requires only the

is not required. Also in the test method is the recommendation that the kinetic results are confirmed using an isothermal aging test which is based on first order kinetics. The analyses may be applied more generally: the problem of assigning the isothermal law has been discussed by both authors. Critical to the determination of the kinetic parameters is the measurement of temperature which must be as precise as possible. It is essential to calibrate the temperature scale over the range of heating rates used in the measurements.

The analytical procedures developed by Coats and Redfern (5) and Borchardt and Daniels (6) were judged to be the best by Barendregt (7). The conclusion was based on a study of a liquid sample in which self-heating is likely to be less than with solids. A comparison was made between the results from a variety of dynamic procedures and that firmly based on isothermal experiments. Both analyses were used with first order kinetics but can accommodate a variety of isothermal laws. A careful assessment of experimental errors is needed when attempting to assess the isothermal law. An advantage claimed for these analyses is that they require only a single thermal analysis curve. They may be carried out simultaneously with the ASTM procedure but the more general use of many different procedures to search for common results seems of dubious scientific merit.

The Borchardt and Daniels procedure has been used widely in the study of solid-state reactions in spite of reservations by the authors. The possible lack of temperature uniformity is equally relevant to other procedures. Ozawa (8) has commented that area measurements may not always provide a sure route to fractional extents of reaction and observed linear relationships not necessarily confirm the kinetic model envisaged in the analysis. It has been recommended

concordance between the results lends assurance that the correct kinetic scheme has been adopted.

The analyses discussed so far are for dynamic experiments. They are divided into differential and integration methods depending on whether the emphasis lies in the use of the differential or integrated forms of the rate equation. Among the differential methods are those of Borchardt and Daniels (6), Freeman and Carroll (9), Ozawa (3) and Kissinger (4). Integration methods include those of Coates and Redfern (5) and Horowitz and Metzger (10). Integration of the Arrhenius term has been discussed by many authors (11, 12) although numerical solutions are well established. The integral $\int_0^T \exp(-E/RT) dT$ may be expressed $\frac{E}{R} \int_x^\infty x^{-2} \exp(-x) dx = \frac{E}{R} p(x)$ where $x = E/RT$. Tables of values of the integral $p(x)$ are available and much of the discussion has been concerned with finding suitable approximations.

The derivation of kinetic parameters from isothermal experiments is less contentious since it approaches the classical route. Part of the initial curve may be 'lost' during the period of equilibration and as a result it is difficult to determine the extent of reaction from area measurements. In contrast, the rate of reaction is well defined since the base line may be determined precisely. We have found the iso-Q line technique (7) easy to use. It allows the Arrhenius activation energy to be determined at fixed extents of reaction and makes no kinetic assumptions other than that kinetics are separable. Isothermal experiments are particularly useful for identifying acceleratory reactions although there may be very long induction periods.

There are now many hundreds of publications dealing with the investigation of reaction kinetics by thermal analysis. For the most part the work is directed towards determining the global kinetics

report there is a comparison between the most popular routes to the kinetic parameters. They have been discussed in the context of differential scanning calorimetry although many were developed originally for thermogravimetry or differential thermal analysis. Amongst recent major reviews on solid-state kinetics are those by Brown, Dollimore and Galwey in Comprehensive Chemical Kinetics (13) and Sestak (14) who deals with the subject in a rigorous and highly mathematical manner. An earlier review of kinetics under non-isothermal conditions was published by Sestak, Satava and Wendlandt (15). Quite different is the review by Carr and Galwey (16) which was described by the authors as 'an experiment in reviewing'. It surveys the literature published in 1981 and contains interesting observations on the part played by thermal analysis.

Appendix

This appendix contains a brief description of 'named' methods for kinetic analyses. It is not concerned with their application to particular compounds. The methods selected are those which are most frequently cited. Some were developed for thermogravimetry and differential thermal analysis but the concern here is only with their application to differential scanning calorimetry.

Abbreviations and Symbols

dynamic	experiment in which the temperature is raised at a uniform rate.
isothermal	experiment in which the temperature is maintained constant.
rate law	dependence of the rate on the extent of reaction and temperature, assumed separable $\frac{d\alpha}{dt} = f(\alpha)g(T)$.
single curve	entire analysis may be carried out using a single thermal analysis curve.
DTA	differential thermal analysis.
TG	thermogravimetry.
A	pre-exponential factor
E	activation energy
f(α)	isothermal rate law
g(T)	temperature dependence of the rate, assumed to be $A \exp(-E/RT)$
T	temperature, T_m temperature of peak maximum
t	time
α	fractional extent of reaction
$(1-\alpha)^n$	'n th' order isothermal law
ϕ	heating rate

1. H.E. Kissinger, 'Variation of Peak Temperature with Heating Rate in Differential Thermal Analysis', J.Res.Nat.Bur.Stand., 57(1956)217.
2. H.E. Kissinger, 'Reaction Kinetics in Differential Thermal Analysis', Anal. Chem., 29(1957)1702.
3. J.P. Elder, 'The General Applicability of the Kissinger Equation in Thermal Analysis', J.Therm.Anal., 30(1985)657.

Dynamic method originally for DTA much criticized but less so for DSC. Alternative method in ASTM E698. Linear relationship between $\ln(\phi/T_m^2)$ and T_m^{-1} , gradient $-E/R$. $f(\alpha) = (1-\alpha)^n$, n from shape index (2), $f(\alpha) = (1-\alpha)$ often assumed. A from criterion for peak maximum $n(1-\alpha)_m^{n-1} = 1 + (n-1)2RT_m/E$ and $E\phi/RT_m^2 = An(1-\alpha)_m^{n-1} \exp(-E/RT_m)$. Application to other rate laws considered in (3).

4. H.J. Borchardt and F. Daniels, 'The Application of Differential Thermal Analysis to the Study of Reaction Kinetics', J.Amer.Chem. Soc., 79(1957)41.

Dynamic method originally for DTA of liquids, widely used, single curve. Linear relationship between $\ln\{\frac{d\alpha}{dt}/f(\alpha)\}$ and $1/T$, gradient $-E/R$, intercept $\ln A$. $f(\alpha)$ by trial and error, $f(\alpha) = (1-\alpha)$ often assumed.

5. G.O. Piloyan, I.D. Ryabchikov and O.S. Novikova, 'Determination of Activation Energies of Chemical Reactions by Differential Thermal Analysis', Nature, 212(1966)1229.

Dynamic method originally for DTA, single curve. Linear relationship between $\frac{d\alpha}{dt}$ and $1/T$, gradient $-E/R$. $f(\alpha)$ not required, assumes change in α insignificant, use initial part of peak $\alpha < 0.4$.

6. E.S. Freeman and B. Carroll, 'The Application of Thermoanalytical Techniques to Reaction Kinetics. The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Monohydrate', J.Phys.Chem., 62(1958)394.
7. B. Carroll and E.P. Manche, 'Kinetic Analysis of Chemical Reactions for Non-Isothermal Procedures', Thermochim.Acta, 3(1972)449.

Dynamic method, originally for TG, single curve only. Linear relationship between $\Delta \ln(\frac{d\alpha}{dt})/\Delta \ln(1-\alpha)$ and $\Delta T^{-1}/\Delta \ln(1-\alpha)$, gradient $-E/R$. Assumes $f(\alpha) = (1-\alpha)^n$, n from intercept. Application to TG has given erroneous results.

8. E.P. Manche and B. Carroll, 'On the Calculation of the Activation Energy for Solid State Reactions', Thermochim.Acta., 25(1978)77.

Isothermal method, linear relationship between $\ln(\frac{d\alpha}{dt})$ and T^{-1} at fixed values of α , gradient $-E/R$. $f(\alpha)$ not required. Avoids effect of lag time on plots of $\ln t$ against T^{-1} . Route to α not specified.

9. A.W. Coates and J.P. Redfern, 'Kinetic Parameters from Thermogravimetric Data', Nature, 201(1964)68.

Dynamic method, originally for TG, single curve. Assumes $f(\alpha) = (1-\alpha)^n$. Linear relationship between $\ln\{[1-(1-\alpha)^{1-n}]/T^2(1-n)\}$ and $1/T$ or when $n = 1$, $\ln\{-\ln(1-\alpha)/T^2\}$ and $1/T$, gradient $-E/R$. n by trial and error with 0, 1/2, 2/3 and 1 as possible values. Other versions available since method depends on approximation introduced for $\int_0^T \exp(-E/RT)dT$.

10. J.H. Sharp and S.A. Wentworth, 'Kinetic Analysis of Thermogravimetric Data', Anal.Chem., 41(1969)2060.

Dynamic method, originally for TG, for DSC takes the same form as (4).

11. T. Ozawa, 'Kinetic Analysis of Derivative Curves in Thermal Analysis', J.Therm.Anal., 2(1970)301.

Dynamic, derivation of $\log \phi = -0.4567E/RT_m + \text{constant}$, ie. linear relationship between $\ln \phi$ and T_m^{-1} , gradient $-0.4567E/R$. A from a comparison between experimental 'master' curves of reduced rate with those calculated assuming $f(x)$. Basis of ASTM E698.

12. T. Ozawa, 'Critical Investigation of Methods for Kinetic Analysis of Thermoanalytical Data', J.Therm.Anal., 7(1975)601.

13. C.E. Doyle, 'Series Approximations to the Equation of Thermogravimetric Data', Nature, 207(1965)290.

Corrections incorporated into (11)

14. J.H. Flynn and L.A. Wall, 'A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data', Polymer Letters, 4(1966)323.

Independent derivation of linear relationship between $\log \phi$ and T_m^{-1} to obtain E (11).

15. J.H. Flynn, 'The Isoconversional Method for Determination of Energy of Activation at Constant Heating Rates', J.Therm.Anal., 27(1983)95.
16. J.M. Criado and A. Ortega, 'A New Approximation of the $p(\alpha)$ Function', Thermochem.Acta., 80(1984)123.

Corrections to the Doyle approximations (13) used in obtaining kinetic parameters from (11) and (14). Alternative approach (16) applicable to values of $E/RT \gg 2$.

17. Yu L. Shiskin, 'Reaction Kinetics Calculated by the Single-Point Method. A Synthesis of the Borchardt-Daniels Theory and Kissinger Theory of Differential Thermal Analysis', J.Therm.Anal., 30(1985)557.

Dynamic, DTA, analyses based on a combination of (1), (2) and (4). Assumes $f(\alpha) = (1-\alpha)^n$, advantages not self-evident.

18. R.N. Rogers and E.D. Morris, 'On Estimating Activation Energies with a Differential Scanning Calorimeter', *Anal.Chem.* 38(1966)412.
19. R.N. Rogers and L.C. Smith, 'Estimation of Preexponential Factor from Thermal Decomposition Curve of an Unweighed Sample', *Anal.Chem.*, 39(1967)1024.
20. R.N. Rogers and L.C. Smith, 'Application of Scanning Calorimetry to the Study of Chemical Kinetics', *Thermochim.Acta.*, 1(1970)1.
21. R.N. Rogers, 'Simplified Determination of Rate Constants by Scanning Calorimetry', *Anal.Chem.*, 44(1972)1336.
22. R.N. Rogers, 'Differential Scanning Calorimetric Determination of Kinetic Constants of Systems that Melt with Decomposition', *Thermochim.Acta* , 3(1972)437.
23. R.N. Rogers and G.W. Daub, 'Scanning Calorimetric Determination of Vapor-Phase Kinetics Data', *Anal.Chem.*, 45(1973)596.

Dynamic, single curve. Simple treatment (18) takes same form as (5). A from peak maximum $A = \phi E \exp(E/RT_m)/RT_m^2$ (19) assuming $f(\alpha) = (1-\alpha)$. For $f(\alpha) = (1-\alpha)^n$, linear relationship between $(1-\alpha) \frac{d^2\alpha}{dt^2} / (\frac{d\alpha}{dt})^2$ and $(1-\alpha) / \frac{d\alpha}{dt} T^2$, gradient $E\phi/R$ and intercept $-n/\alpha$ (20). Need to identify melting (22) and vapour phase reaction (23). Isothermal, single curve, linear relationship between $\ln(\frac{d\alpha}{dt})$ and t , gradient $-k$, for $f(\alpha) = (1-\alpha)$ (21).

24. H.H. Horowitz and G. Metzger, 'A New Analysis of Thermogravimetric Traces', *Anal.Chem.*, 35(1963)1464.
25. A.J. Kassman, 'An Approximation to the Linear Heating Rate in Non-Isothermal Kinetics', *J.Therm.Anal.*, 18(1980)199.

Dynamic, originally for TG, $f(\alpha) = (1-\alpha)^n$, $\int_0^T \exp(-E/RT)dT$ replaced by $\frac{RT_r^2}{E} \exp\{-\frac{E}{RT_r}(1-\frac{\delta T}{T_r})\}$ where T_r refers to suitable reference point on curve eg. maximum, $\delta T = T-T_r$ which must be small. For peak maximum $1-\alpha_m = n^{1/(1-n)}$ if $n \neq 1$ and $1-\alpha_m = \frac{1}{e}$ if $n = 1$ which allows n to be established. Plot $\ln \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ against δT to obtain a straight line with a gradient E/RT_r^2 . Alternative approach (25), linear relationship between $\ln \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ and $1/T$, gradient $\{-E/R+2T_m\}$.

26. H.M. Hauser and J.E. Field, 'New Method for TG and DSC Data Analysis', *Thermochim.Acta.*, 27(1978)1.

Dynamic, mainly for TG, DSC by analogy, numerical integration of $d\alpha/dt$ to yield α at time t . Best-fit $\ln d\alpha/dt - \ln f(\alpha)$ against $1/T$ to obtain $E, A, f(\alpha)$.

References

1. M. Singh, 'Thermal Hazard Evaluation by Differential Scanning Calorimetry', M.Sc. thesis, University of Leeds, 1986.
2. J. Sestak and G. Berggren, *Thermochim. Acta*, 3(1971)1.
3. T. Ozawa, *J. Therm. Anal.*, 2(1970)301.
4. H.E. Kissinger, *J.Res.Nat.Bur.Stand.*, 57(1956)217.
5. A.W. Coats and J.P. Redfern, *Nature*, 201(1964)68.
6. H.J. Borchardt and F. Daniels, *J.Amer.Chem.Soc.*, 79(1957)41.
7. R.B. Barendregt, 'Thermal Investigation of Unstable Substances Including a Comparison of Different Thermal Analytical Techniques', Thesis, Technische Hogeschool, Delft, Holland, 1981.
8. T. Ozawa, *J.Therm.Anal.*, 7(1975)601.
9. E.S. Freeman and B. Carroll, *J.Phys.Chem.*, 62(1958)394.
10. H.H. Horowitz and G. Metzger, *Anal.Chem.*, 35(1963)1464.
11. J.H. Flynn, *J.Therm.Anal.*, 27(1983)95.
12. J.M. Criado and A.Ortega, *Thermochim.Acta*, 80(1984)123.
13. M.E. Brown, D.Dollimore and A.K.Galwey, 'Reactions in the Solid State', *Comprehensive Chemical Kinetics*, Vol.22, Elsevier, Amsterdam, 1980.
14. J. Sestak, 'Thermophysical Properties of Solids', *Comprehensive Analytical Chemistry*, Vol.XIID, Elsevier, Amsterdam, 1984.
15. J. Sestak, V. Satava and W.W. Wendlandt, *Thermochim.Acta*, 7(1973)447.
16. N.J. Carr and A.K. Galwey, *Thermochim.Acta*, 79(1984)323.

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