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THE MEASUREMENT OF MEANINGFUL ACTIVATION ENERGIES
Using thermoanalytical methods. A tentative proposal

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The uncertainty surrounding the significance of the measured kinetic parameters of solid state decomposition reactions is discussed briefly. Some suggestions are made about what precautions should be taken in order to favour the measurement of undistorted results. Some criteria are proposed for deciding whether a measured E value can be considered to have its usual meaning. The results of a series of experiments aimed at measuring the activation energy of the decomposition of calcium carbonate using a variety of methods, sample sizes and experimental conditions are presented. These results are compared with results found in the literature and it is concluded that it is possible to measure a reproducible value for E and it is tentatively proposed that this value is meaningful in terms of the energy barrier model of chemical reaction kinetics.

When the Arrhenius equation is applied to solid state decomposition reactions the following expression is usually employed

$$\frac{d\alpha}{dt} = f(\alpha)Ae^{-E/RT} \tag{1}$$

where t = time, T = absolute temperature, α = fraction decomposed, $f(\alpha)$ some function that is characteristic of the way in which the reaction proceeds, A = the pre-exponential factor, and E = the activation energy. Accordingly the influence of temperature on the reaction rate is expressed through the value of a single parameter, E. The meaning of E is generally interpreted in terms of the well known energy barrier model of chemical reaction kinetics and a given chemical reaction should have a characteristic "energy barrier" or activation energy. However, Dollimore, Galway and Brown in their recent review of reactions in the solid state [1] noted that "the kinetic parameters most frequently used to provide information about the (reaction) step identified as rate limiting are A and E. Values for nominally the same chemical change often show significant deviations". The existence of these significant deviations together with the often observed dependence of the shape of thermogravimetric curves on experimental conditions [2–4], poses a serious problem which has led several authors to conclude that it is not generally appropriate to interprete the measured kinetic behaviour of solid state reactions in terms of the energy barrier model. It is argued [5] that the existence of the mass and energy transport problems inherent in highly endothermic reactions of the type solid → solid + gas precludes the measurement of the real value of E (although some authors have raised theoretical objections to the use of the Arrhenius equation itself [6]). Under this supposition the activation energy becomes a formal or operational parameter devoid of physical significance that primarily reflects the experimental conditions under which the experimental data were gathered.

In order to resolve the problem of whether the measurement of meaningful activation energies is possible or whether it is only possible to measure formal values we must answer two questions:

i) which experimental methods and conditions favour the measurement of meaningful E values and

ii) what criteria should be used for deciding whether a measured E value is meaningful?

In answer to the first question, an inspection of the literature suggests that the following three precautions would seem advisable:

(a) Rejection of methods based on a single rising temperature experiment [7, 8];

(b) The partial pressure of the product gas in the sample environment should be as low as possible especially for reversible reactions [9–14];

(c) Sample masses should be as low as possible to minimize self-cooling effects.

As a partial answer to the second question we would like to propose the following criteria:

(a) Independence of sample size: establishing a sample mass below which the activation energy is independent of sample size is a necessary but not sufficient condition for believing that the value of this parameter has its usual meaning;

(b) Independence of experimental method: for a simple reaction it would seem reasonable to assume that it should be possible to find the same activation energy using:

(i) different heating programmes and

(ii) vacuum and flowing inert atmosphere experiments.

If this is possible it suggests that temperature and pressure gradients have not dominated the behaviour of the reactant as changing both i) and ii) changes the mass and energy transport conditions within the sample bed. In general, therefore, finding the same value for E using a variety of methods (while respecting the three precautions given above) can be taken as evidence that this parameter is meaningful;

(c) Independence of particle size distribution: just as the activation energy should be independent of the sample mass it should also be independent of the sizes of the individual grains of a powdered sample.

It is possible to propose a large number of reasons why the simple form of the Arrhenius equation given above might prove inadequate when dealing with complex systems. It is also possible to invent many criteria and conditions that must be met before doubts concerning the significance of the measured kinetic parameters of solid state decomposition reactions can be resolved. The way in which the surface area changes with extent of decomposition and temperature, the effect of temperature on the crystallinity of both reactant and product etc. . . can all be brought into play. The three criteria proposed above are best considered as preliminary guide-lines aimed principally at establishing whether mass and energy transfer problems are significantly distorting the measured E values of a simple decomposition reaction.

In this article we investigate the possibility of meeting the proposed criteria for the ostensibly simple case of the thermal decomposition of calcium carbonate whilst conforming as far as possible to the three precautions given above. In the context of the influence of sample size it is interesting to note that Criado et al. [15] found that results obtained using Constant Rate Thermal Analysis (CRTA) were not greatly influenced by sample size. Here we present the results of a study of the influence of sample size on activation energies measured using the CRTA method to examine whether it is possible to meet the "independent of sample size" criterion. We go on to compare these results with those obtained using the isothermal and linear rising temperature methods under both flowing inert atmosphere and vacuum conditions to examine whether it is possible to meet the "independence of experimental method" criterion. Finally a brief examination of the influence of particle size distribution is made.

Experimental methods

In accordance with the suggested precautions only vacuum and flowing inert atmospheres were used to maintain product gas partial pressure around the sample as low as possible. No results based on the analysis of a single rising temperature experiment are presented here. Except during the study on the effect of sample size, sample masses never exceeded 10 mg as this was considered to be the lowest sample size concomitant with high accuracy.

All the results were obtained using gravimetric equipment. Results obtained under vacuum, including the CRTA results, were obtained using a Mettler Thermoanalyzer N° 76, the CRTA method and apparatus have been described previously. The results obtained under flowing nitrogen were obtained using a Stanton Redcroft TG 750.

Materials

Prolabo analytical grade precipitated $CaCO_3$, British Oxygen white spot nitrogen.

1) Rate jump constant rate thermal analysis

A series of jumps between two predetermined reaction rates, both of which were maintained constant, were carried out and the corresponding temperature jumps were measured. From Eq. (1) E can be calculated by

$$E = \ln \left[\frac{\left(\frac{d\alpha}{dt}\right)_1 \Big/ \left(\frac{d\alpha}{dt}\right)_2}{\frac{1}{T_2} - \frac{1}{T_1}} \right] \tag{2}$$

2) Constant rate thermal analysis

A series of experiments were carried out at different constant decomposition rates. For a series of values of α (the same value of α in each experiment) a plot was made of

$$\ln \left(\frac{d\alpha}{dt}\right) \quad \text{against} \quad \frac{1}{T}$$

which, from Eq. (1) gives a slope of $-E/R$.

3) Isothermal method

For isothermal experiments Eq. (1) can be integrated to give

$$g(\alpha) = Ae^{-E/RT}t \tag{3}$$

where

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) \tag{4}$$

A series of isothermal experiments were carried out, then, for a series of values of α (the same values in each experiment), a plot was made of

$$-\ln(t) \quad \text{against} \quad \frac{1}{T}$$

which from Eq. (3) gives a slope of $-E/R$.

4) Linear rising temperature method

The integral form of Eq. (1) for linear rising temperature experiments can be expressed as

$$g(\alpha) = \frac{AR}{bE} T^2 e^{-E/RT} I(E, T) \tag{5}$$

where b = the heating rate,

$$I(E, T) = 1 - \frac{2!}{E/RT} + \frac{3!}{(E/RT)^2} - \ldots \tag{6}$$

A series of rising temperature experiments were carried out at different heating rates. For a series of values of α (the same values in each experiment) a plot was made of

$$\ln\left(\frac{b}{T^2 I(E,T)}\right) \text{ against } \frac{1}{T}$$

which, from Eq. (5), gives a slope of $-E/R$ (this is effectively a modified Ozawa method). The series $I(E,T)$, see Eq. (6), was evaluated using an iterative procedure described by Whitehead et al. [16] which avoids errors that might arise from using inaccurate approximations to the exponential integral.

It should be noted that all these methods avoid assuming any particular form for $f(\alpha)$. Methods 2, 3 and 4 all involve conducting a series of experiments using different samples then the values of some function at a given value of α (the same value in each experiment) are plotted against $1/T$. The same series of values of α was used in all cases, $\alpha = 0.1$ to 0.9 in steps of 0.1.

Results

1) Effect of sample size using the CRTA method

Figure 1 shows a plot of E against α for a series of experiments carried out at a regulated pressure of 5×10^{-5} Torr using Rate Jump CRTA. Sample sizes of 100 mg, 200 mg and 300 mg were used. For the 100 mg and 300 mg experiments a rate jump ratio, i.e. $(d\alpha/dt)_1/(d\alpha/dt)_2$, of 7.1 was used. For the 200 mg sample a series of ratios was used which corresponds to the divisions marked on the graph as follows: (a) 7.1, (b) 5.2, (c) 2.7 and (d) 3.4. It can be seen that all the results are in good agreement except for slightly lower values of E for $\alpha < 0.1$. The averages and standard deviations are given in Table 1; results for values of α lower than 0.1 were excluded to avoid bias

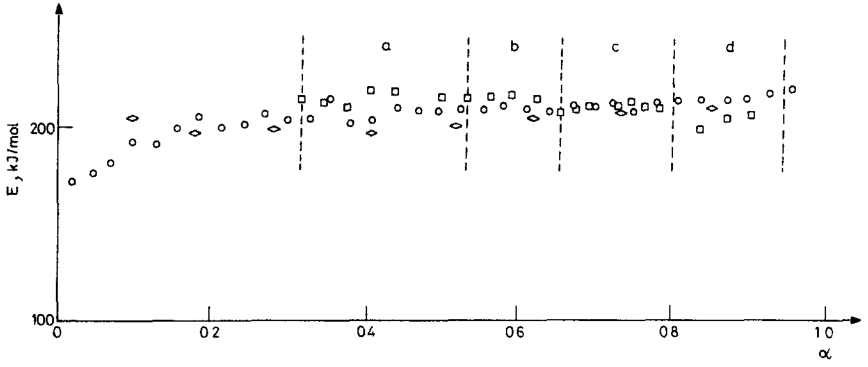

Fig. 1 Rate jump constant rate results. ◇ = 100 mg, □ = 200 mg, ○ = 300 mg

Table 1 Activation energies for the decomposition of $CaCO_3$

Sample mass, mg	Method	No. of experiments or rate jumps	Atmosphere	E, kJ mol^{-1}	Standard deviation	Average linear regreassion coefficient
100 mg	Rate jump	8	5×10^{-5} torr	205	4.9	–
200 mg	Rate jump	21	5×10^{-5} torr	214	4.6	–
300 mg	Rate jump	31	5×10^{-5} torr	211	6.4	–
500 mg	Rate jump	52	5×10^{-5} torr	205	13.9	–
10 mg	CRTA	4	5×10^{-5} torr	210	9.0	0.998180
10 mg	Isothermal	3	$< 5 \times 10^{-4}$ torr	199	8.0	0.999068
10 mg	Rising temp.	4	$< 5 \times 10^{-4}$ torr	191	15.5	0.989451
10 mg	Isothermal	4	N_2 200 ml/min	217	2.7	0.999259
10 mg	Rising temp.	3	N_2 200 ml/min	196	12.3	0.998767
10 mg	Isothermal	4	N_2 20 ml/min	188	1.3	0.989618
10 mg	Rising temp.	4	N_2 20 ml/min	213	7.5	0.996530
10 mg*	Isothermal	6	N_2 200 ml/min	209	2.4	0.997029
10 mg*	Rising temp.	4	N_2 200 ml/min	214	9.7	0.997816

* Sample sieved between 53–45 μm.

when comparing these results with those obtained using other methods which did not include measurements in the interval of α from 0 to 0.1. A further experiment was carried out using a 500 mg sample again using a regulated pressure of 5×10^{-5} Torr and a rate jump ratio of 7.1. The results from this experiment were more scattered than those of the other rate jump experiments and this fact is expressed in the wider standard deviation (see Table 1).

When using the rate jump method the time taken to execute the jump must be very small in comparison to the total duration of the experiment. The duration of the experiment is directly proportional to the mass of the sample. Thus it is difficult to use the jump method with very small sample sizes. For this reason the non-jump method, method 2, was used when the sample mass was reduced to 10 mg. Four different reaction rates were used; 1.683×10^{-4}/sec., 8.333×10^{-5}/sec., 5.669×10^{-5}/sec. and 2.671×10^{-5}/sec., at a regulated pressure of 5×10^{-5} Torr. Nine straight lines were plotted corresponding to the nine selected values of α, the results are presented in Table 1.

2) The effect of the experimental method

A series of isothermal and rising temperature experiments were carried out under vacuum (pressure never greater than 5×10^{-4} Torr) and under dry flowing nitrogen. Preliminary experiments established that the shapes of mass loss curves were influenced by the nitrogen flow rate. For this reason two nitrogen flow rates were used, the maximum practical flow rate of 200 ml/min. and a slow flow rate of 20 ml/min.

Heating rates between 0.5 and 6 deg./min. were used in all cases as it was found that available heating rates above 6 deg./min. gave results that significantly departed from the straight line Arrhenius plots obtained with heating rates within these limits.

Every series of isothermal experiments covered a temperature interval wider than 40°. In all cases nine plots were made corresponding to the nine selected values of α in the range 0.1 to 0.9 inclusive.

In Table 1 the average activation energies are presented toegther with the standard deviations and the average linear regression coefficients for the nine plots.

Generally the rising temperature results gave slightly increasing or decreasing values for the activation energy with increasing values of α. These trends were not observed with isothermal results or with CRTA results and must be considered as spurious.

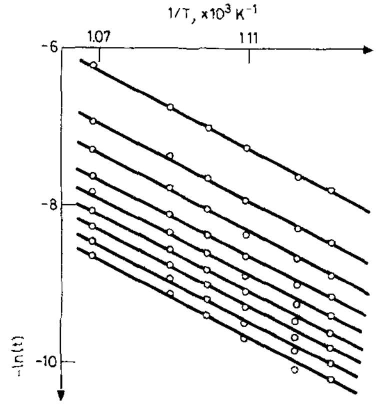

Fig. 2 Isothermal results 10 mg $CaCO_3$ (sieved between 53–45 μm) under flowing nitrogen at 200 ml/min

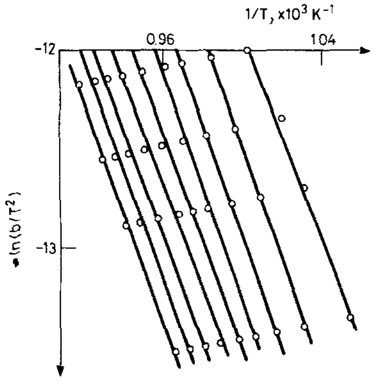

Fig. 3 Rising temperature results 10 mg $CaCO_3$ (sieved between 53–45 μm) under flowing nitrogen at 200 ml/min

3) The effect of particle size distribution

A calcium carbonate sample was sieved between 53–45 μm, a fraction which represents less than 10% of the total by weight. A series of isothermal and rising temperature experiments were carried out using the sieved samples under flowing dry nitrogen. The results are presented in Table 1. Figures 2 and 3 show the plots obtained using these sieved samples. A comparison of the average regression coefficients shows that the linearity of these Arrhenius plots can be taken as fairly typical of the other results.

Discussion of results

The CRTA results are in good agreement giving standard deviation intervals which all overlap. There is no clear relationship between the variations in sample size and the measured activation energies despite the wide range of sample sizes used, 10 mg to 500 mg. In addition the rate jump results are independent of the size of the rate jump thus indicating that the Arrhenius equation correctly predicts the relationship between reaction rate and temperature. It should be noted that this series of experiments encompasses a range of temperatures from 740 K to 990 K and a range of decomposition rates that extends from a rate which corresponds to a total reaction time of 31 days to a rate which corresponds to a total reaction time of 1 5 hours. Despite this wide variation the small observed differences, between average *E* values are within anticipated experimental errors and they change with sample size in an apparently random fashion. In addition these results are in excellent agreement with the previously determined value of Rouquerol [17].

A study has been made by Gallagher and Johnson [18] on the effect of sample size using the isothermal method. They carried out a series of experiments in which they reduced the sample mass from 32 to 1 mg without finding a sample size below which the activation energy remained invariant. Instead they found a linear relationship between log (sample mass) and *E* which they extrapolated to obtain a value of 175 kJ for a 500 mg sample. This relationship is purely empirical and has no theoretical bases. Clearly it does not apply to results obtained using the CRTA method. We therefore suggest that it is an artefact of the isothermal method used under the experimental conditions these authors adopted. It seems possible that the CRTA method enables the virtual elimination of errors arising from mass and energy transport problems due to the fact that it maintains the product gas pressure at a low and constant value and also maintains the decomposition rate very low (and consequently reduces self-cooling effects). Thus with this method it is possible to fulfil the "independence of sample size" criterion.

The agreement between the results obtained using the CRTA method and those obtained using other methods is also quite good. The variations shown in Table 1 are apparently random, i.e. rising temperature results are not systematically higher or lower than isothermal results, and the agreement between vacuum and flowing atmosphere results is good. Sieving the sample had no significant effect on the measured activation energy. The fact that the observed variations are random implies that they originate purely from experimental errors which change in a complex way with changing methods and sample environment. We therefore propose that by using small sample sizes (< 10 mg) it is possible to fulfil, to within a reasonable degree of accuracy, the "independence of experimental method" and "independence of particle size distribution" criteria for a meaningful E value.

Table 2 shows a selection of literature values for the activation energy of the thermal decomposition reaction of calcium carbonate. It clearly illustrates the significant deviations refered to in the introduction. If we examine Table 2 critically and, in accordance with the proposed precautions, i) exclude results based on single rising temperature experiments, ii) select those results obtained under vacuum or flowing atmospheres free of carbon dioxide, and iii) exclude all results obtained with sample masses greater than 100 mg (necessarily a somewhat arbitrary choice) we obtain Table 2 where it can be seen that the agreement between the remaining results is quite good.

Table 2 Literature activation energies for the decomposition of calcium carbonate

Reference	E, kJ mol^{-1}	Sample weight, mg	Atmosphere	Method *
a)				
20	170	250	N_2	RT
19	146–176	500	vacuum	I
21	216	100	air	RT
22	172	300–450	N_2	I
23	163	290	air	RT
24	170	455	air	I
25	397	500–2000	air	I
26	184	100	N_2	RT
27	180–192	1000	–	RT
17	201–217	100	vacuum	JCRTA
28	565–3828	1–16	CO_2	RT
29	142–297	1–16	O_2	RT
13	213–226	4	Ar	RT
13	950	4	5% CO_2 in Ar	I
13	607–715	4	5% CO_2 in Ar	RT
13	2046–2155	4	CO_2	RT
b)				
29	190–208	1–32	O_2	I
13	201	4	Ar	I
30	205	35–70	vacuum	I
31	210–212	10**	N_2	SRT

* Methods are as follows: I = Isothermal, RT = single Rising Temperature experiment, SRT = several Rising Temperature experiments, JCRT = Jump Constant Rate Thermal Analysis.

** Sample size supplied by Authors.

If the activation energy is considered to be in the region 210±10 kJ mol^{-1} then this is a reasonable value compared to the value of the enthalpy of formation of $CaCO_3$ which is about 177 kJ mol^{-1} [19].

Conclusion

To within a reasonable degree of accuracy the results presented in Table 1 together with the literature values given in Table 2 fulfil the three criteria for meaningfulness proposed in the introduction to this article. We tentatively propose, therefore, that the activation energy of the thermal decomposition of calcium carbonate is in the range 210±10 kJ mol^{-1} and that the value of this parameter can be interpreted in terms of the energy barrier model of chemical kinetics.

We found that changing experimental conditions and methods did change the kinetic behaviour of this reaction but these changes were expressed as changes in $f(\alpha)$ and A rather than E. This point shall be discussed in a future article.

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Zusammenfassung — Die sich auf die Signifikanz gemessener kinetischer Parameter von Zersetzungsreaktionen fester Stoffe beziehende Unsicherheit wird kurz diskutiert. Es werden einige Vorschläge hinsichtlich der Vorkehrungen unterbreitet, die zu treffen sind, um unverfälschte Meßergebnisse zu erhalten. Einige Kriterien werden vorgeschlagen, die geeignet sind zu entscheiden, ob ain gemessener E-Wert die übliche Bedutung hat. Ergebnisse einer Reihe von Experimenten werden angegeben, die ausgeführt wurden, um die nach verschiedenen Methoden, bei Anwendung unterschiedlicher Probenmengen und unter verschiedenen Versuchsbedingungen für die Aktivierungsenergie der Zersetzung von $CaCO_3$ erhaltenen Werte zu vergleichen. Es wird gefolgert, daß es möglich ist, den Wert von E reproduzierbar zu messen, und versuchsweise vorgeschlagen, diesen Wert als sinnvoll für das Energiebarrierenmodell der chemischen Reaktionskinetik anzusehen.

Резюме — Кратко обсуждена неопределенность измеренных значений кинетических параметров реакций разложений твердых тел. Высказаны предложения о тех предосторожностях, которые должны быть приняты во внимание с целью измерения неискаженных результатов. Предложены некоторые критерии для решения того, что измеренное значение E может быть истинным. Представлены результаты ряда экспериментов, проведенных с целью измерения различными методами энергии активации реакции разложения карбоната кальция, изменяя размеры образцов и экспериментальные условия. Полученные результаты сопоставлены с литературными данными и сделано заключение о возможности измерить воспроизводимое значение энергии активации. Условно предложено, что такое значение является средним в зависимости от модели энергетического барьера кинетики химической реакции.