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THE DETERMINATION OF KINETIC PARAMETERS FOR SOME SOLID STATE REACTIONS

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The kinetics of many solid state reactions can best be explained in terms of an order of reaction; this is particularly true in the case of polymer degradation. The methods currently available for the determination of n and k, from isothermal data, are either limited in the range of α which can be used or are difference–difference techniques where the data must of necessity be highly accurate. This paper presents a review of these methods and introduces a new approach by which n and k can be obtained directly, giving results which are unique and objective in that they provide a best fit to the experimental data.

In studies on the thermal decomposition of solid materials, it is frequently found that the kinetics of the process may best be described in terms of an "order of reaction". The concept of reaction order, in the context of solid state reactions, has led to much discussion and there is some argument as to whether it may, or may not, be applied to the decomposition reactions of inorganic materials. In the case of polymer degradation, however, it is frequently found that melting of the sample occurs prior to decomposition. This leads to the formation of an essentially homogeneous system and the use of reaction order to describe the kinetics of reaction is widely used.

Certain reaction orders, however, can be derived from theoretical considerations and thus have physical significance for systems where the sample is in the form of discrete particles, rather than a homogeneous liquid. The two most frequently encountered are the cases where the reaction order, n, has the values of one half or two thirds. These equations relate to the movement of a reaction interface through a disc or sphere, respectively. In many instances, however, values of the reaction order may well lie in between these two idealised extremes and it is probable that values other than one half or two thirds reflect deviations of sample geometry away from the perfect disc or sphere.

This paper presents a brief survey of the concept of reaction order as applied to solid state reactions, together with methods for its determination. Some of the methods available for the determination of n have been published elsewhere, but a new approach will be described in which the order may be calculated directly from the experimental data. This method is without the usual limitations on the range of decomposition which may be considered.

Experimental

The experimental system chosen for investigation was the isothermal decomposition under vacuum of the octahydrates of strontium and barium hydroxide to form the corresponding monohydrates. Only brief details of the experimental results will be given here in so far as the data has been used in developing the methods for determining the reaction order; a fuller account of the kinetics of this process is to be published elsewhere [1].

The apparatus used initially was a quartz spring balance details of which have been described before [2]. However this proved unsuitable for studying the kinetics of the dehydration process and the reasons for this will be discussed later. The majority of the experiments were carried out using a C. I. microbalance, model 2B, manufactured by C. I. Electronics, Salisbury, England. A continuous record of sample weight as a function of time was obtained by feeding the balance output signal into a 1 mV potentiometric recorder. The microbalance could take a maximum sample weight of 500 mg with the weight being measured to a sensitivity of ca. 0.05 mg on the most sensitive range used.

Results and discussion

A typical isothermal weight loss plot is shown in Fig. 1; this refers to the dehydration of a sample (23 mg) of barium hydroxide octahydrate at 23° under vacuum. As can be seen, the process is deceleratory throughout with no apparent induction period. The weight loss obtained (39.4%) agrees well with the theoretical figure (39.9%) for formation of the monohydrate. (The fact that the stable crystalline monohydrate is formed, and its X-ray powder pattern, has been described elsewhere [3].)

Sharp et al. have published [4] a useful method for obtaining qualitative information regarding kinetic mechanisms. Their method involves comparing experimental data, in the form of plots of α (the reactive fraction decomposed) versus $t/t_{0.5}$ (where $t_{0.5}$ is the time at which α equals 0.5), with theoretical curves for nine commonly encountered kinetic equations.

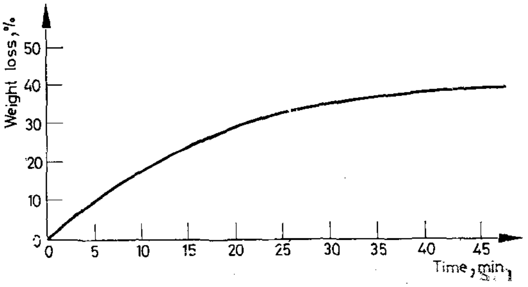

Fig. 1. Isothermal vacuum dehydration of barium hydroxide octahydrate (23 mg)

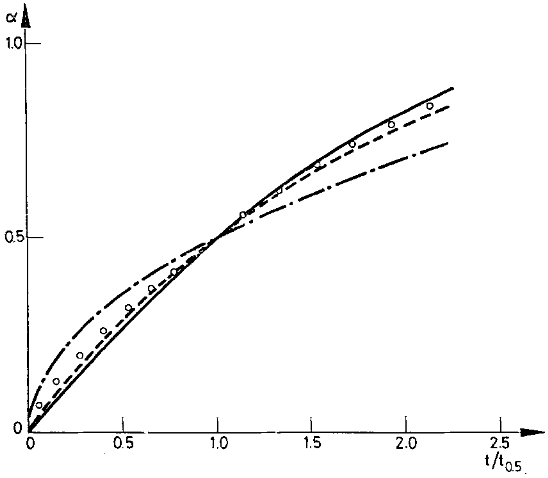

Fig. 2. Reduced time plot for isothermal dehydration of barium hydroxide octahydrate (500 mg). ——— theor. curve for $n = 1/2$; - - - - - theor. curve for $n = 2/3$; — · — · — · theor. curve for first order diffusion process; ○ ○ ○ expt. data

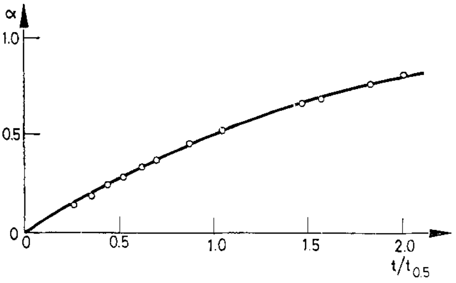

Fig. 3. Reduced time plot for barium hydroxide octahydrate (23 mg). ——— theor. curve for $n = 2/3$; ○ ○ ○ expt. data

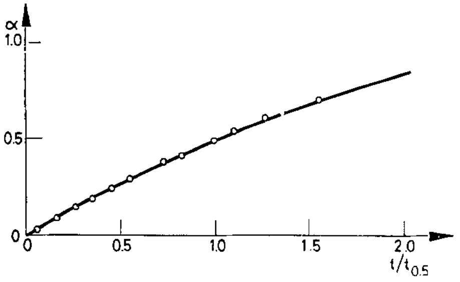

Fig. 4. Reduced time plot for compacted sample barium hydroxide octahydrate. ——— theor. curve for $n = 1/2$; ○ ○ ○ expt. data

This method was therefore applied to our experimental data; the first attempt used the results obtained on the spring balance for the dehydration of a large sample (ca. 500 mg) of barium hydroxide octahydrate. It can be seen (Fig. 2) that the data gives a reasonable fit to an equation of the reaction interface type (where n has a value somewhere between one half and two thirds) over the α range 0.3 to 0.8. Below $\alpha = 0.3$ there is strong evidence to suggest that diffusional effects are affecting the reaction mechanism. It was assumed that the presence of a densely packed sample was causing this apparent diffusion control at low α values and therefore the experiment was repeated using the microbalance with a 23.0 mg sample of the barium hydroxide. When this data was put into the form of α versus $t/t_{0\,5}$, it can be seen (Fig. 3) that there is a very close fit to the two thirds order law. If a sample of the barium salt was viewed under a high power microscope then the crystals appeared to have the form of small distorted octahedra. This strongly suggests that the physical shape of the crystals is controlling the reaction process.

If this assumption was correct, then it would be expected that compacting a sample of the barium hydroxide into a thin disc would lead to the dehydration process obeying the one half order law. Fig. 4 shows the α versus $t/t_{0.5}$ plot for the dehydration of a thin disc (1 mm × 13 mm dia.) of barium hydroxide octahydrate and, as can be seen, a good fit to the contracting disc equation ($n = 1/2$) is obtained. (Above $\alpha = 0.70$, the data is incomplete, since at this point the pellet disintegrated.)

With the corresponding strontium hydroxide, it was found that dehydration of a 23.0 mg sample was best described by the contracting disc equation. Using this material it was necessary to grind the solid before the dehydration experiments since the sample in the bottle was in the form of large lumps. When the ground material was viewed under the microscope it was found that the crystals had a plate like form and thus the value of a reaction order of one half is not unexpected, if once again sample shape is assumed to control the mechanism of decomposition.

However, even though the experimental data, using the small sample weights, gave values of n which were apparently close on one half and two thirds, it was felt desirable to determine the actual value of n. This was even more necessary in the case of the large sample of barium hydroxide octahydrate, where the value of n was certainly not one of the theoretical figures.

In general, the equation which relates the rate of reaction to the amount of substance present, for a reaction of order n is:

$$\frac{-\,\mathrm{d}(a-x)}{\mathrm{d}t} = k'(a-x)^n \tag{1}$$

where k' is the rate constant,
a is the original concentration of the substance,
x is the amount reacted in time t.

Integrating equation (1)

$$-\int_{a}^{a-x} \frac{\mathrm{d}(a-x)}{(a-x)^{n}} = k' \int_{0}^{t} \mathrm{d}t \tag{2}$$

so that

$$-\left[\frac{(\alpha-x)^{1-n}}{1-n}\right]_{a}^{a-x} = k't \quad \text{when } n \neq 1\ , \tag{3}$$

in other words

$$a^{1-n} - (a-x)^{1-n} = k't(1-n)\,. \tag{4}$$

This can be rearranged to give

$$1 - \left(\frac{a-x}{a}\right)^{1-n} = kt(1-n) \tag{5}$$

where $k = k'/a^{(1-n)}$, so that the dimension of k is always time^{-1} Now

$$\frac{a-x}{a} = 1 - \frac{x}{a} = 1 - \alpha$$

where α is the fraction decomposed and $(1 - \alpha)$ is the fraction of the reactant remaining.

Thus equation (5) becomes

$$1 - (1-\alpha)^{1-n} = kt(1-n)\,.] \tag{6}$$

Equation (6) is the generalised rate equation for a reaction of order n when $n \neq 1$.

When $n = 1$, equation (1), on integration, yields the simple first order kinetics form

$$\ln(1-\alpha) = -kt\,. \tag{7}$$

The two equations which have been referred to earlier are the cases when $n = 1/2$

$$\text{ie}\ \ 1 - (1-\alpha)^{1/2} = \frac{kt}{2} \tag{8}$$

and when $n = 2/3$

$$\text{ie}\ \ 1 - (1-\alpha)^{1/3} = \frac{kt}{3}\,. \tag{9}$$

Equations (8) and (9) are often referred to as the contracting disc and the contracting sphere equation, respectively. These correspond to the movement of a reaction interface through disc or spherical shaped particles. The equations have been deduced from geometric considerations regarding particle shape and sample packing. In the majority of practical systems it is unlikely that the experimental conditions will exactly correspond to the theoretical situation and therefore it is not unreasonable to suppose that values of n other than one half or two thirds will be obtained.

Sharp et al. [4] have pointed out, when discussing their method for deducing the mechanism of kinetic processes, that great care must be taken in distinguishing between reactions which follow one half or two thirds order kinetics. It is especially difficult to differentiate between the two mechanisms for α values below 0.50. A closer inspection of equation (6) will show that it is important that the value of n be known accurately since the value of k is dependent upon it.

It is not possible to obtain the value of the reaction order by simple graphical means from the integrated rate equation (6). Several methods have been suggested, but these are generally restricted in the range of α which can be used.

If equation (6) is rearranged in the form:

$$(1-\alpha)^{1-n} = 1 + (n-1)kt$$

then the left hand side may be expanded as a binomial series. If terms in α^3 and higher order are neglected then this reduces to:

$$\frac{1}{k} + \frac{n\alpha}{2k} = \frac{t}{\alpha}. \tag{10}$$

Thus a plot of t/α versus α should yield both n and k from the values of the slope and intercept.

MacCallum and Schoff [5] report that equation (10) is not very satisfactory even for values of α less than 0.25: our own attempts at using it also tend to support this view.

These authors have suggested that an improved method of calculation may be made as follows.

Equation (10) can be rewritten in the form:

$$\frac{1}{k} = t/[\alpha(1 + n\alpha/2)]. \tag{11}$$

The term $(1 + n\alpha/2)^{-1}$ can be expanded, and if terms in α^2 and higher orders of α are dropped, then one obtains the relationship:

$$\frac{t}{\alpha} = \frac{1}{k} + \frac{nt}{2}. \tag{12}$$

Equation (12), often termed the Wilkinson Equation, appears to give a much better approach for the determination of n and k. MacCallum and Schoff [5] have compared equations (10) and (12) and find that (12) is more widely applicable to the polymer systems they have studied. Even so, the range of α that can be used in either of these methods is limited to $\alpha < 0.30$ by the approximations which have been made in the calculation.

A method which can be used over the whole decomposition range has been derived [6] from the Mampel Intermediate Law which is equivalent to the general integration of equation (2):

$$1-(1-\alpha)^{1/n'}=kt+b \tag{13}$$

where b is a constant,
and n' is a reaction order which is related to the n used in equation (6) by

$$n'=\frac{1}{1-n}\,.$$

Then

$$\frac{-\,\mathrm{d}(1-\alpha)}{\mathrm{d}t}=\frac{k}{1/n'}(1-\alpha)^{1-1/n'} \tag{14}$$

If $\dfrac{k}{1/n'}$ is replaced by k''

then equation (14) becomes

$$\frac{-\,\mathrm{d}(1-\alpha)}{\mathrm{d}t}=k''(1-\alpha)^{1-1/n'}\,. \tag{15}$$

Taking logs

$$\log\left(\frac{-\,\mathrm{d}(1-\alpha)}{\mathrm{d}t}\right)=\left(1-\frac{1}{n'}\right)\log\,(1-\alpha)+\text{constant}. \tag{16}$$

Thus a plot of $\log\left(\dfrac{-\mathrm{d}(1-\alpha)}{\mathrm{d}t}\right)$ vs. $\log(1-\alpha)$ should give a straight line of slope $1-1/n'$, so that n can be calculated.

This method suffers from the disadvantage of being a difference-difference technique, that is, differences between successive values of $1-\alpha$ are taken. Therefore any error in a single value of α will affect two values of $\dfrac{\mathrm{d}(1-\alpha)}{\mathrm{d}t}$. Since the reaction order is determined from the slope of the graph then the scatter of the points will lead to uncertainties in the correct value of n. This is illustrated in Fig. 5 which is the $\log\left(\dfrac{-\,\mathrm{d}(1-\alpha)}{\mathrm{d}t}\right)$ versus $\log(1-\alpha)$ plot for the data already described for strontium hydroxide octahydrate, where $n=1/2$. As can be seen the

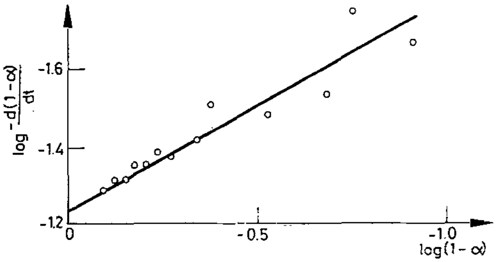

Fig. 5. Reaction order plot for the isothermal dehydration of a sample of strontium hydroxide octahydrate (23 mg) using the method given by equation (16)

plot shows considerable scatter and a least squares best fit to the points gives a value of $n = 0.43$.

In general, most workers assume that n is going to have a value of either one half or two thirds and therefore experimental data for α and t is usually substituted into the contracting disc (8) or contracting sphere (9) equations. The results are then plotted in the form of $1 - (1 - \alpha)^{1-n}$ versus t and the one which gives the best linear graph is assumed to hold for the reaction under consideration. Fig. 6 shows a plot of $(1 - \alpha)^{1-n}$ versus t for values of n = one half and two thirds. The data used are some test data where n was given a value of 0.6. As can be seen, the plots are essentially linear over a wide range of α, thus making it difficult to obtain, by this graphical method, an accurate value of n.

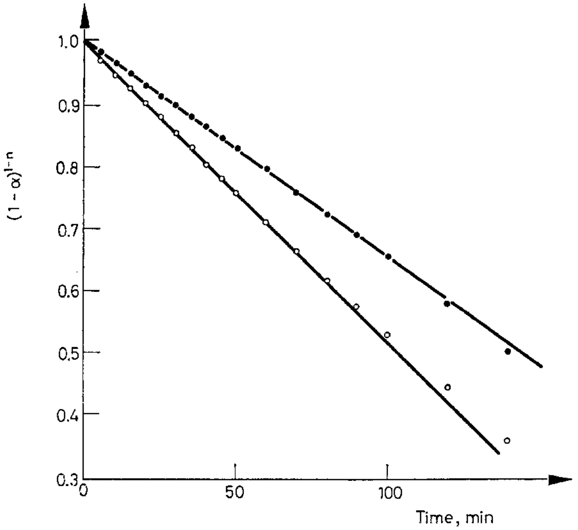

Fig. 6. Typical rate plot for the determination of reaction order. α data calculated from equation (6) with $k = 0.01$ and $n = 0.60$; full points $n = 2/3$; open points $n = 1/2$

We have therefore approached the problem of the determination of n and k from a different direction. Equation (6) may be rewritten in the form:

$$\alpha = 1 - [1 - kt(1 - n)]^{1/(1-n)} \tag{17}$$

Values of n and k may be best determined using a least square criterion in which the sum of the squares of the differences (residuals) between the observed and calculated values of α is minimized i.e.

$$\min R = \sum_{i=1}^{p} (\alpha_{i(\mathrm{expt})} - \alpha_{i(\mathrm{calc})})^2$$

where there are p sets of α, t data.

The minimisation is complicated by the non-linear occurrence of n in the equation for α. However, if initial values of k and n can be found which are reasonably close to the true values, then this complication can be avoided by expanding the function for α in a linear Taylor series around the initial estimates $k^{(0)}$ and $n^{(0)}$. Thus

Table 1

Test data with α, expt. and calculated, using a value of $n = 0.50$ and $k = 0.010$

Determination of k and n

Cycle	k	n	SUMRSQ
1	0.01500000	0.60000000	0.29353607
2	0.00628106	0.29978247	0.36372003
3	0.00930471	0.43409559	0.00431444
4	0.00992605	0.49541570	0.00005252
5	0.00998810	0.49902622	0.00000107
6	0.00998848	0.49904730	0.00000107
7	0.00998848	0.49904728	0.00000107

Data calculated with consistent values of k and n

Time	α, expt.	α, calc.	Residual error
10.0	0.0970	0.0973	0.0003
15.0	0.1440	0.1442	0.0002
20.0	0.1900	0.1898	−0.0001
25.0	0.2340	0.2341	0.0001
30.0	0.2770	0.2772	0.0002
35.0	0.3190	0.3190	0.0000
40.0	0.3600	0.3596	−0.0003
45.0	0.3990	0.3990	0.0000
50.0	0.4370	0.4371	0.0001
60.0	0.5100	0.5096	−0.0003
70.0	0.5770	0.5771	0.0001
80.0	0.6400	0.6396	−0.0003
90.0	0.6970	0.6971	0.0001
100.0	0.7500	0.7497	−0.0002
110.0	0.7970	0.7972	0.0002
120.0	0.8400	0.8398	−0.0001
130.0	0.8770	0.8773	0.0003
140.0	0.9100	0.9099	−0.0000

$$\alpha(t, k, n) = \alpha(t, k^{(0)}, n^{(0)}) + \frac{\partial \alpha}{\partial k^{(0)}} \delta k^{(0)} + \frac{\partial \alpha}{\partial n^{(0)}} \delta n^{(0)} \tag{18}$$

where
$$\delta k^{(0)} = k - k^{(0)}$$
$$\delta n^{(0)} = n - n^{(0)}$$

and k and n are the true values.

Table 2

Comparison of experimental and calculated values of α for the isothermal, vacuum dehydration of $Sr(OH)_2 \cdot 8H_2O$ (23.0 mg)

Determination of k and n

Cycle	k, min^{-1}	n	SUMRSQ
1	0.07000000	0.70000000	0.06133210
2	0.03493081	0.33735271	0.26021637
3	0.05049742	0.43643068	0.00177051
4	0.05302324	0.49652536	0.00024913
5	0.05325691	0.49965263	0.00023171
6	0.05325719	0.49963426	0.00023170

Data calculated with consistent values of k and n

Time, min	α, expt.	α, calc.	Residual error
3.0	0.146	0.153	0.007
4.0	0.197	0.201	0.004
5.0	0.245	0.248	0.003
6.0	0.293	0.294	0.001
7.0	0.337	0.338	0.001
8.0	0.381	0.380	−0.000
9.0	0.422	0.421	−0.000
10.0	0.464	0.461	−0.002
13.0	0.578	0.572	−0.005
15.0	0.638	0.639	0.001
17.0	0.703	0.700	−0.002
20.0	0.789	0.781	−0.007
22.0	0.823	0.828	0.005
25.0	0.885	0.888	0.003
30.0	0.960	0.959	−0.000

The least squares principle then allows $\delta k^{(0)}$ and $\delta n^{(0)}$ to be calculated from two linear, simultaneous equations obtained by setting

$$\frac{\partial R}{\partial k^{(0)}} = 0 \quad \text{and} \quad \frac{\partial R}{\partial n^{(0)}} = 0 \, .$$

Improved estimates of k and n are then formed

$$k^{(i)} = k^{(0)} + \delta k^{(0)}$$
$$n^{(i)} = n^{(0)} + \delta n^{(0)}$$

Table 3

Comparison of experimental and calculated values of α for the isothermal, vacuum dehydration of a compacted sample of $Ba(OH)_2 \cdot 8H_2O$

Determination of k and n

Cycle	k, min^{-1}	n	SUMRSQ
1	0.00700000	0.65000000	0.19738786
2	0.01269823	0.51840595	0.04141141
3	0.01052705	0.48714221	0.00098843
4	0.01062677	0.50149927	0.00100622
5	0.01064700	0.50682337	0.00102528
6	0.01065441	0.50890989	0.00103311
7	0.01065737	0.50974795	0.00103631
8	0.01065858	0.51008806	0.00103762
9	0.01065907	0.51022666	0.00103816
10	0.01065927	0.51028325	0.00103838
11	0.01065935	0.51030637	0.00103846

Data calculated with consistent values of k and n

Time, min	α, expt.	α, calc.	Residual error
5.0	0.030	0.052	0.022
10.0	0.088	0.103	0.015
15.0	0.157	0.153	—0.003
20.0	0.196	0.201	0.005
25.0	0.239	0.248	0.009
30.0	0.289	0.293	0.004
40.0	0.384	0.380	−0.003
45.0	0.422	0.421	—0.000
55.0	0.495	0.498	0.003
61.0	0.551	0.542	−0.008
70.0	0.610	0.604	−0.005
85.0	0.700	0.698	−0.001

and the process repeated until the changes in successive values of the corrections are less than predetermined amounts.

This technique has previously been used for the calculation of rate constants [7, 8], but has found little application in the determination of reaction order and does not appear to have been applied to the field of solid state decompositions at all. Naturally, convergence of the iterative method is not guaranteed, but the choice of good starting values of k and n is seldom a problem. In the case of the hydroxide decompositions n is in the range 0.3 to 0.7 and rapid convergence is obtained by using an initial value of $n = 0.5$ to estimate k from equation (17).

The considerable advantage of the method is that it provides values of k and n which are unique and objective, in the sense that they produce a "best fit" to the data and do not reflect the preference of the experimenter for a particular

Table 4

Comparison of experimental and calculated values of α for the isothermal, vacuum dehydration of $Ba(OH)_2 \cdot 8H_2O$ (23.0 mg)

Determination of k and n

Cycle	k, min^{-1}	n	SUMRSQ
1	0.05000000	0.45000000	0.00724485
2	0.05156643	0.56420923	0.00057784
3	0.05201875	0.59143181	0.00040420
4	0.05205168	0.59325599	0.00040632
5	0.05205211	0.59328321	0.00040636
6	0.05205212	0.59328355	0.00040636

Data calculated with consistent values of k and n

Time, min	α, expt.	α, calc.	Residual error
3.0	0.139	0.148	0.009
4.0	0.187	0.195	0.008
5.0	0.234	0.240	0.006
6.0	0.280	0.283	0.003
7.0	0.324	0.325	0.001
8.0	0.365	0.366	0.001
10.0	0.445	0.442	−0.002
12.0	0.518	0.513	−0.004
17.0	0.671	0.666	−0.004
18.0	0.697	0.692	−0.004
21.0	0.769	0.764	−0.004
23.0	0.809	0.806	−0.002
25.0	0.844	0.843	−0.000
27.0	0.873	0.875	0.002
30.0	0.908	0.916	0.008

order of reaction. As a result, the parameters have increased theoretical significance and comparisons with the results of other workers are made more valid.

In order to check the validity of the method a set of test data was prepared in which k and n were given values of 0.010 and 0.500, respectively. Values of α were then calculated for set time intervals using equation (6). The results obtained are shown in Table 1. It can be seen that when the data are fitted well by the form of equation (6) then the minimum in the residual sum of squares (SUMRSQ in the tables) occurs at the converged values of k and n. Also, the differences between the experimental and predicted values of α are distributed randomly.

Calculated and experimental values for the decomposition of $Sr(OH)_2 \cdot 8H_2O$ (where initial work using the $t/t_{0.5}$ plot indicated $n = 0.5$) and a compacted sample of $Ba(OH)_2 \cdot 8H_2O$ (initial $n = 0.5$) are shown in Tables 2 and 3. Once again, a good fit to the experimental data is obtained with values of n, calculated, of 0.5 and 0.51 respectively.

If the data contain a systematic error, for example, the time at which the reaction commences is in error by a fixed amount (a not uncommon occurrence) then the minimum in the residual sum of squares occurs prior to convergence and the residual errors are distributed systematically. This can be illustrated by a consideration of the data obtained on the dehydration of a sample (23.0 mg) of barium hydroxide octahydrate where the $t/t_{0.5}$ plot had indicated a value of n = two thirds. The converged values of k (0.052 min^{-1}) and n (0.593) give a good fit to the data but the differences between α_{expt} and α_{calc} pass from positive through negative to positive again. The present work is directed towards making corrections for such systematic errors and towards assigning accuracies to the estimated parameters. A more comprehensive discussion of this method and others under development is to be published in the near future [8].

Conclusion

A method has been developed in which it is possible to calculate 'best fit' values of k and n directly from α, time data. The technique enables one to obtain the unique values and thus provides useful assistance in the determination of the kinetics of reactions which can be described in terms of a reaction order.

Note

The calculations presented in this paper were performed on an ICL 4130 computer using the program SOLITER. This program was written in ALGOL 60.

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Résumé — Pour de nombreuses réactions dans l'état solide l'ordre de réaction constitue un très bon moyen pour exprimer leur cinétique; c'est le cas, en particulier, de la dégradation des polymères. Les différentes méthodes dont on dispose pour déterminer n et k à partir des données isothermes sont limitées à l'intervalle d'utilisation de α ou opèrent par différences successives ce qui nécessite des données très précises. L'article présente une revue de ces méthodes et introduit une nouvelle approche où n et k peuvent être obtenus directement, en donnant des résultats uniques et objectifs qui assurent un meilleur accord avec les données expérimentales.

Zusammenfassung — Die Kinetik vieler Reaktionen in fester Phase kann am besten an Hand einer Reaktions-Ordnung erklärt werden; dies besteht besonders bei dem Abbau von Polymeren. Die für die Bestimmung von n und k aus isothermen Daten zur Verfügung stehenden Methoden sind entweder auf den verwendbaren Bereich von α beschränkt oder sind Differenz–Differenz-Methoden, bei welchen es äußerst genauer Angaben bedarf. Die vorliegende Veröffentlichung gibt eine Übersicht dieser Methoden und führt eine neue Annäherung ein, durch welche n und k unmittelbar erhalten werden können. Diese Methode ergibt einzigartige und zielgerechte Ergebnisse, indem diese sich den Versuchsdaten am besten anpassen.

Резюме — Кинетика многих твердофазных реакций лучше всего объясняется на основании реакции первого порядка; это особенно справедливо в случае распада полимеров. Методы, часто употребляющиеся для определения n и, k основаны на изотермических данных. Методы либо ограничены в области α, либо используют методику «разница - разница», при которой данные должны быть очень точными. В настоящей работе дан обзор этих методов и новый подход, с помощью которого можно непосредственно получить n и k. Полученные результаты являются объективными и единственными в своем роде и они наилучшим образом подходят к экспериментальным данным.