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# THE DETERMINATION OF KINETIC PARAMETERS FOR REACTIONS INVOLVING SOLIDS

A.C. NORRIS, M.I. POPE and M. SELWOOD

*Department of Chemistry, Portsmouth Polytechnic, Portsmouth (Gt. Britain)*

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## ABSTRACT

Reactions involving solids are normally characterised by the rate constant, $k$, and the apparent order of reaction, $n$; certain values of $n$ are consistent with simple physical models for the reaction mechanism. However, for most solid decompositions, only $n = 0.67$ can provide a realistic interpretation of the process. Determination of $n$ by the method of non-linear least squares analysis from thermoanalytical data leads typically to values of $n$ ranging from 0.2 to 0.6, for single stage, solid decompositions. With the aid of computer simulation, these results have been ascribed to asymmetry of the reaction interface. It is shown that evaluation of $k$ is insensitive to the reaction order for realistic values of $n$. It is also clear that the shape of the reaction interface cannot be elucidated by substituting arbitrary values of $n$ in the contracting interface equation, so as to obtain a rectilinear graph.

The mechanism of a solid state reaction usually passes through three consecutive stages, not all of which may be observed experimentally. If the fraction of solid reacted at time $t$ is $\alpha$, then for very low values of $\alpha$ (typically $\alpha << 0.05$) the predominating mechanism involves nucleation of the new phase at separate points on the solid surface. These nuclei grow in size until they eventually merge so as to form a continuous reaction interface, which normally contracts as it advances through the solid particles. It is this contracting interface mechanism which generally provides the observed experimental data for values of $\alpha$ ranging typically from about 0.1 to 0.9. During the final stages of the reaction, diffusion of gases through the bed of decomposed reactant may eventually become rate determining.

In practice the reaction interface does not move forward uniformly, but advances more rapidly where the crystal structure is strained, or distorted, i.e. along dislocation lines. Hence the actual interface is often extremely ragged and therefore impracticable to represent by a simple, physical model.

Reactions involving solids are normally characterised by the rate constant, $k$, and the so-called "order of reaction", $n$. Certain values of $n$ are consistent with simple physical models representing the reaction mechanism; however, the fact that a particular value of $n$ is obtained from the experimental data does not prove that the corresponding model correctly describes the course of the reaction.

Values of $n$ to which particular significance is often attached are as follows:

$n = 0.00$ corresponds to a reaction occurring uniformly over the surface of an infinite plane, with no contraction of the area of the reaction interface. It is assumed that the rate of reaction is not inhibited by diffusion through the layer of solid reaction product;

$n = 0.50$ is consistent with a disc contracting inwards at its circumference only. Reaction at the plane surfaces (which represent most of the exposed surface area) is not taken into account;

$n = 0.67$ is the value expected for a contracting sphere, or cube, where the reaction interface advances at an identical rate along all crystal planes. Equally with a packed bed of amorphous, or microcrystalline powder, where the reaction interface advances uniformly in all dimensions, $n$ would again be expected to assume a value of 0.67;

$n = 1.00$ is usually associated with a reaction occurring in a homogeneous liquid phase. This may be either because the sample is above its melting point, or because a low melting eutectic has formed between the reactant and product at the reaction interface. This latter situation may occur much more frequently than might be imagined, and has been the subject of an extensive investigation by Berg et al. [1].

Now the case where $n = 0.00$ is virtually confined to the study of thin films, while only compounds with a layer lattice structure might be expected to react exclusively at their edges (leading to $n = 0.50$). Similarly, the value of $n = 0.67$ should only arise if the crystals (or corresponding packed bed of powder) are isodimensional. Such idealised conditions are seldom met in practice, so that for most solid state reactions there can be no justification for assuming that the kinetic data will accord to one of the above values of $n$. Nevertheless, a search of recent literature still reveals numerous statements to the contrary, of which the following is typical: "Thermal decomposition processes of solid components belong to the group of first order reactions" [2].

In order to characterise the kinetics of a reaction involving a solid from thermoanalytical data, the procedure generally adopted has been to substitute selected values of $n$ into a suitable rate equation [3—12]. The idealised values of $n$ are usually assigned; the true order of reaction is then taken as the value of $n$ which results in a rectilinear graph between an appropriate function of a sample variable and time.

More recently, methods of data analysis have been developed [13,14] which impose no pre-conditions on either $k$ or $n$, except for setting upper and lower limiting values. Application of this procedure under carefully controlled experimental conditions [15] has led to values of $n$ ranging between ca. 0.2 and 0.5 for two solid state decomposition reactions. These results suggest that the actual value assigned to $n$ by this procedure is in fact a weighted mean of the theoretically significant values previously discussed. To illustrate this point, we have assumed that real crystals behave as if they were constructed from a combination of tiny cubes and planar surfaces. The former might be expected to give rise to a reaction order of 0.67 while the latter would be associated with $n = 0.00$. Consequently our composite crystal, consisting of both cubic and planar regions, might intuitively be supposed to exhibit a decomposition reaction order lying between these two limiting values, i.e. $0.00 < n < 0.67$. The actual order would reflect the relative contributions of cubes and planes to the overall structure.

In order to test this hypothesis, we have used a computer to generate 21 sets of exact time ($t$)/mass ($M$) data from the contracting interface equation

$$M_t = M_\infty + (M_0 - M_\infty)[1 - kt(1-n)]^{1/1-n}$$

where the subscripts refer to sample mass at time 0, $t$ and $\infty$. $M_0$ is assigned the numerical value 10.0, $M_\infty = 5.0$, $k = 0.01$ and $t$ is divided into 0, 5, 10, ..., 100 arbitrary time units. Curves were then plotted of sample mass remaining against time, with $n$ being given values of 0.00 and 0.67, respectively (Fig. 1). The differing contributions which the cubic and planar regions of the crystal might make to the overall kinetic parameters are taken into account by constructing a median between the two original curves. Two further curves were then drawn, each midway between the median and the two original curves. Analysing the three new mass/time curves by the method of nonlinear least squares [13] yields the following kinetic parameters.

| | $k$, recovered | $n$, recovered | $Q(k, n)$ |
|---|---|---|---|
| Lower quartile | 0.0098 (0) | 0.0787 (33) | $4.95 \times 10^{-5}$ |
| Median | 0.0098 (0) | 0.2049 (55) | $7.97 \times 10^{-5}$ |
| Upper quartile | 0.0098 (0) | 0.3932 (53) | $4.34 \times 10^{-5}$ |

$Q(k, n)$ is the error sum of squares, and numbers in parentheses indicate the standard deviation, e.g. 0.0787 (33) means 0.0787 ± 0.0033.

The small and closely similar error terms indicate that the newly constructed curves correspond well with data for a contracting interface mecha-

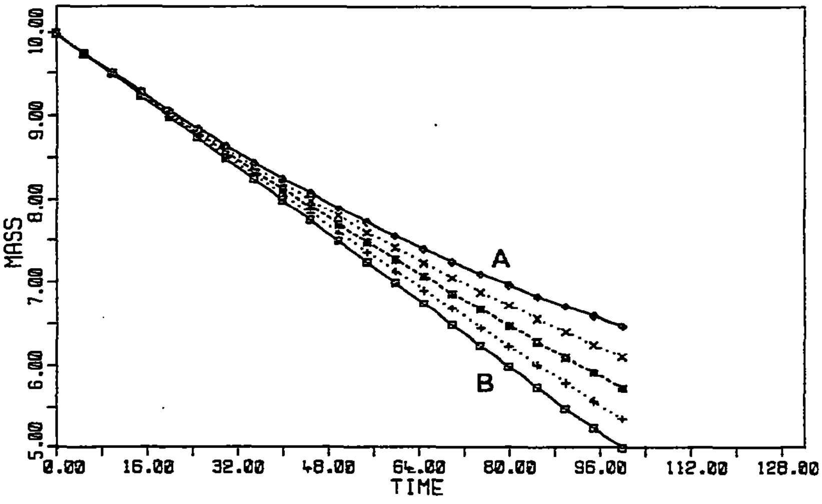

Fig. 1. Hypothetical mass/time curves calculated for a solid state decomposition reaction, where the reaction order is (A) 0.67 and (B) 0.00. The broken lines represent the median and curves intermediate between the median and the two original plots.

nism. It will be seen that the values of *k* are recovered with high accuracy and are identical; in contrast *n* increases five-fold between the lower and upper intermediate curves. The probable effect of particle shape on the decomposition reaction order is thus apparent.

This result demonstrates the importance of placing no pre-conditions, other than feasible bounds, on the values of *k* and *n*. In particular it shows that *k* is relatively insensitive to the exact value of *n*; however, it is not possible to draw conclusions concerning the reaction mechanism, or particle shape, from the apparent linearity of graphs obtained using only selected, idealised values of *n*.

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