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ANALYSIS OF ISOTHERMAL KINETIC DATA FROM SOLID-STATE REACTIONS

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In most solid state reactions the reaction velocity can be described as a product of two functions $K(T)$ and $f(1 - \alpha)$ where T is the temperature and α the degree of conversion of the solid reactant. The physical interpretation of these functions is discussed, and a systematic method is described by which $f(1 - \alpha)$ of a reaction is identified from its kinetic data. $K(T)$ and the reaction mechanism are then determined. This method has been successfully applied to analyse the kinetics of the thermal decomposition of silver azide.

In a solid-state reaction, the reaction velocity is given by $-\mathrm{d}/\mathrm{d}t\ (1 - \alpha) = \dot{\alpha}$, where $\alpha = \alpha(t)$ is the fraction of the solid reactant which has reacted by time t. Its kinetics can be solved by determining $\dot{\alpha}$ as a function of temperature and the global amount of reactant left. This phenomenological knowledge is a necessary, though not sufficient, condition for elucidating the reaction mechanism. It is necessary to formulate the reaction velocity in terms of the global variable α, because there is a continuous collapse of structure in the reactant. Furthermore, the local concentration of the reactant varies throughout the reaction volume and cannot be used as a state variable. In fact, unlike the case of a homogeneous reaction in the liquid or gaseous phase, there is no real 'reaction order' with respect to any reactant in a reaction involving condensed matter whose mechanism is usually of the heterogeneous type.

If the reaction proceeds isothermally, it is observed empirically that (α, t) curves corresponding to different temperatures T are isomorphic to one another, at least within a range of T, i.e., by a linear scale change in t, different curves can be superimposed [1]. It follows that $\dot{\alpha}$ is a separable function:

$$(\dot{\alpha})_{\text{isothermal}} = K(T)f(1 - \alpha). \tag{1}$$

Here $f(1 - \alpha)$ may change in different ranges of T or α. For every $f(1 - \alpha)$, there corresponds a single $K(T)$. It should be noted that experimental data may be adequately analysed by (1) only if it has been ensured that the temperature distribution in the sample is sufficiently uniform and constant. Furthermore, the theoretical significance of $K(T)$ and $f(1 - \alpha)$ determined from the data should always be examined with regard to the class of mechanisms they indicate. A question of consistency arises in this respect. In the literature, coherent and integrated accounts of the physical (as contrasted with the formal) meanings of $K(T)$ and $f(1-\alpha)$ are not easily found. A discussion on their interpretations therefore forms the first part of this paper. In the second part we propose an efficient method of determining, with confidence, both $f(1-\alpha)$ and $K(T)$ from $\dot{\alpha}$ and $\alpha(t)$ data. The interpretation of $f(1-\alpha)$ is the essential link in this method between the experimental data and the functions.

Physical interpretations

The function $f(1-\alpha)$

Solid-state reactions are complex processes which proceed in several stages. These can be the delocalization or transfer of electrons in chemical bonds (in the case of non-metals), the diffusion of atoms, free radicals, or ions, the desorption of product molecules when they are in the gaseous phase, the heat transfer to the reaction zone in the case of endothermic reactions, and the formation of a new solid structure (crystalline or amorphous) if one of the products is in the solid phase. The last step may often be further differentiated into nucleation, growth of nuclei (at velocities which depend on sizes of nuclei) [1] and sometimes the collapse of the lattice from a transitory one to the equilibrium structure [2]. Irrespective of the details of reaction mechanisms, however, under a given set of circumstances (T, α, sample history etc.) one of the stages will be the slowest. It then acts as the rate limiting step of the reaction, and it will determine the kinetics i.e., the rate law in (1).

Further, a solid-state reaction has, in contrast to a homogeneous reaction whose progress is independent of spatial coordinates, an additional controlling factor, namely topochemistry. This refers to the geometrical shape of the solid reactant and, in different cases, to its free surface area, its defect structure, the thickness of the product layer if solid, or to the product-reactant boundary, etc.

The function $f(1-\alpha)$ reflects the nature of the rate-limiting step and the topochemistry of the reaction. It may accordingly depend on certain sample conditions, such as whether the sample has been pre-irradiated or bleached, and whether the sample is in the form of a powder, or a large single-crystal of a different shape from the crystallites. It will vary in several ranges of T if in each of them a different elementary step becomes rate-limiting, as occurs in the decomposition of potassium azide [3]. At a given temperature, it may also change in different ranges of α, due to the switching of the rate-limiting step or topochemical changes. This happens, for instance, in the oxidation of zirconium [4] and in most decomposition processes [1]. An extreme case is the decomposition of ammonium perchlorate which, in the two temperature regimes below and above 620K, has entirely different reaction mechanisms and in fact yields different reaction products [5]. In such cases there may be competing paths for the chemical reaction or it may in fact be followed by another chemical reaction whose 'onset temperature' is higher. In all possibilities, however, $f(1-\alpha)$ should be the same for a given α

independent of T (within a range) if it is to have more than only an empirical significance.

In Table 1 we have collected together the more common forms of $f(1-\alpha)$ which have been used in the literature, and the corresponding integrated forms $\int_0^t dt\, \dot{\alpha}/f(1-\alpha) = \int_0^\alpha d\alpha/f(1-\alpha) \equiv F(\alpha)$. Note that $F(\alpha) = K\ (t - t_0)$ if the range of α for which it becomes applicable starts at $\alpha = \alpha(t_0)$. Also, for simplicity hereafter we write K for $K(T)$.

In many reactions, such as most decompositions and dehydrations, the rate-limiting step takes place at the interface between different phases as in sublimation. The speed at which the interface moves into the reactant is (at a given temperature) then either a constant, or a unique function of the interfacial area. This area therefore, from the kinetic point of view, plays the same role as that of concentration in homogeneous reactions. If the speed is constant, then the theoretical significance of $f(1-\alpha)$ is clear: it gives the area expressed as a fraction of the original area at $\alpha = 0$. This is the case of a reaction controlled by the movement of a coherent phase-boundary and listed as F, G and H in Table 1. In this situation, the explicit form of $f(1-\alpha)$ depends on the geometry of the reacting system, though generally it is a decreasing function of α or at most constant.

If the reaction consists of the formation of compact nuclei of a solid product at localized places in the reactant followed by their relatively rapid growth, then, to express the total interfacial area, $f(1-\alpha)$ is derived from the laws of nucleation and growth. This is the situation when the reaction is autocatalytic [13]: reactant molecules at a reactant-product interface react in preference to those at a reactant-'vacuum' surface. The preference is due to the existence of microstrains in the reactant at the interface, or due to the electrochemical potential of the product phase when the rate-limiting step is a redox process. The various possible forms of $f(1-\alpha)$ for an autocatalytic reaction are listed in Table 1, A to E. Note that they have the general form $f(1-\alpha) = \alpha^p(1-\alpha)^q$. In A, B and E, q is zero and α increases monotonically with α. Such a situation is most unlikely to last up to $\alpha = 1$. These types of $f(1-\alpha)$ therefore may apply only to the acceleratory part, if it is present in the α-time curve and which will usually be followed by a decay part. In C and D, q is non-zero and these types give sigmoid-shaped curves. The inflexion point occurs at $\alpha' = p/(p+q)$, as can be seen at once from the condition $\ddot{\alpha} = 0$. It is thus kinetically feasible for them to fit the complete experimental curve. There are, however, physical grounds to consider that even they should be used to analyze only the acceleratory period [1].

In other reactions the rate-limiting step is not confined to, or does not only occur at, the reactant surface. For instance, in the unimolecular-decay type of reaction, all molecules whether on the surface or in the bulk have an equal probability per unit time of reacting. This is the case when the change from the reactant to the solid product phase involves little re-arrangement of the reactant atoms. The reaction has homogeneous mechanism and thus a true reaction order of one, i.e. $f(1-\alpha) = 1-\alpha$. Many decomposition reactions tend to this

Table 1

The common types of solid-state reaction

Reaction	
Autocatalytic	Power-law nucleation and growth at constant speed: *A*
	Linear branching chain of nuclei, no overlap during growth: *B*
	Branching-chain nucleation, interference during growth: *C*
	Random nucleation, growth accompanied by ingestion of nuclei: *D*
	Instantaneous nucleation, size-dependent growth: *E*
Phase-boundary controlled decay	1-dimensional: *F*
	2-dimensional: *G*
	3-dimensional: *H*
Unimolecular decay: *I*	
Diffusion-controlled	1-dimensional: *J*
	2-dimensional: *K*
	3-dimensional: *L*

	$f(1-\alpha) = \dot{\alpha}/K$	$F(\alpha) = Kt$	$m^{\text{i)}}$	Reference
A	$\alpha^{1-1/n}$	$n\alpha^{1/n}$	$\approx 1.27n$	[6]
B	α	$\ln\alpha - C(T)$	ii)	[7]
C	$\alpha(1-\alpha)$	$-\ln\{-(1-1/\alpha)\} -$ $- C_0$	ii)	[8]
D	$\{-\ln(1-\alpha)\}^{1-1/n}(1-\alpha) \simeq$ $\simeq \alpha^{1-1/n}(1-\alpha)^b$	$n\{-\ln(1-\alpha)\}^{1/n}$	n	[9, 10] iii)
E	$\alpha^{3/2}$	$2(\alpha_0^{-1/2} - \alpha^{-1/2})$	ii)	[11]
F	1	α	1.24	[3]
G	$(1-\alpha)^{1/2}$	$2\{1-(1-\alpha)^{1/2}\}$	1.11	
H	$(1-\alpha)^{2/3}$	$3\{1-(1-\alpha)^{1/3}\}$	1.07	[12]
I	$1-\alpha$	$-\ln(1-\alpha)$	1	[13]
J	$1/\alpha$	$\alpha^2/2$	0.62	[14]
K	$1/\{-\ln(1-\alpha)\}$	$\alpha + (1-\alpha)\ln(1-\alpha)$	0.57	[14]
L	$1/\{(1-\alpha)^{-2/3} - (1-\alpha)^{-1/3}\} \simeq$ $\simeq 3(1-\alpha)^{1/3}/\{-\ln(1-\alpha)\}$;	$3\{1-(1-\alpha)^{1/3}\}^2/2$	0.54	[15] iv)
	$1/\{(1-\alpha)^{-1/3} - 1\} \simeq$ $\simeq 3/\{-\ln(1-\alpha)\}$	$3\{1-(1-\alpha)^{2/3}\}/2 -$ $- \alpha$	0.57	[16] iv)

i) Log $\{-\ln(1-\alpha)\} \simeq$ Constant + $m \log t$, $0.15 < \alpha < 0.5$

ii) Plot of L.H.S. in i) against log t distinctively concave upwards; C_0 and α_0 are constants while $C(T)$ is function of temperature

iii) $b = 0.774, 0.700, 0.664, 0.642, \ldots, 0.556$ for $n = 2, 3, 4, 5, \ldots \infty$

iv) Alternative derivations; we have obtained the approximate forms of $f(1-\alpha)$ by expanding into series $(1-\alpha)^{-2/3}$ and $(1-\alpha)^{-1/3}$ to second order in α: resulting error $\simeq \alpha^2/6$ (<10% for $\alpha < 0.8$)

limit at high α values. Another example is when the rate-limiting step is the migration of product ions along the dislocation network to form additional growth nuclei at dislocation nodes [17]. This leads to $f(1-\alpha)=\alpha$, the same form as for branching nuclei [7]. The slow process of 'ageing' in some explosives when they are stored at room temperature may be by such a nucleus-chain mechanism. A third category consists of reactions controlled by the diffusion of reactants across a product layer which is solid. The diffusion may proceed uniformly through the bulk of the layer and is thus structure-insensitive, or preferentially along its gross lattice imperfections arising from product-reactant mismatch. In the case of uniform diffusion, the speed at which the product-reactant interface moves is a function only of the product thickness (and temperature), and the appropriate forms of $f(1-\alpha)$ are included in Table 1 as J, K and L. The oxidation of metals often follows diffusion-controlled kinetics; in sheet form these tarnish according to the parabolic law $\alpha^2 \propto t$. Exceptions aret hose metals in Groups Ia and IIa of the Periodic Table. Excluding beryllium, they all form oxide layers which are porous, so that the atoms of the metal do not have to diffuse through a coherent layer before coming into contact with oxygen.

The function K(T)

It is almost always the case that the temperature-dependent part of (1) can be represented successfully by: –

$$K(T) = K_\infty \exp(-E/kT) \tag{2}$$

in which k is Boltzmann's constant, and the macro-kinetic constants E and K_∞ do not depend on T (within the range), though usually they take on different values when $f(1-\alpha)$ changes.

If it is established that the reaction is rate-limited by a diffusion or migration process, the interpretation of $K(T)$ is complicated, but obviously it is proportional to the corresponding transport coefficient, which in general is an exponential function of T. An over-simplified theory for the situation of uniform one-dimensional diffusion gives $K(T)=(S/V_0)^2 D(T)$, where S is the interfacial area, V_0 the initial volume of the reactant, and $D(T)$ the diffusion coefficient (cf. [19]).

For a single-solid-reactant reaction which is controlled by a surface process, on the other hand, the simple theory of Shannon [18] is often successful. This theory is a generalization of the Polanyi–Wigner equation. Assuming the existence of some activated complex, which as a transition state can be treated in thermodynamic equilibrium with the reactant, he related the pre-exponential factor K_∞ to the rotational and other internal degrees of freedom of a reactant molecule in addition to the vibrational ones. Following Shannon we can set: –

$$K_\infty = (kT/h)\exp(\Delta S^\ddagger/k) \quad \delta S_0/V_0 \tag{3}$$

and

$$\exp(-E/kT) = \exp(-\Delta H^\ddagger/kT). \tag{4}$$

Here the mean-frequency factor kT/h containing Planck's constant is usually in the region of 10^{13} s^{-1} (see below), $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are respectively the entropy and the enthalpy of formation of the transition complex, δ is the thickness of one monolayer and V_0 the initial volume of the reactant, and $S_0 f(1 - \alpha)$ gives the free surface or the product-reactant interface area when the degree of conversion is α. (Strictly speaking, it has been assumed that the reaction proceeds isobarically).

Note that in this interpretation the empirical quantity K_∞ contains the surface-to-volume ratio and so depends on the sample geometry. Also, it is apparently proportional to T. (In gas reactions, the collision theory gives $K_\infty \propto T^{\frac{1}{2}}$.) In our opinion, however, if the vibrational modes are being considered then only at low temperatures will the peak distribution of phonon frequencies lie at kT/h. For most substances (with the exceptions of Be, Cr and diamond) the Debye temperature θ_D is less than 500K, so that the frequency factor should stay as $k\theta_D/h \lesssim 10^{13}$ s^{-1} for all likely experimental temperatures.

The factor $\exp(\Delta S^{\ddagger}/k)$ may alternatively be written in terms of partition functions as $Q^{\ddagger}/Q$, which can be determined from spectroscopic data [20]. In most cases $\Delta S^{\ddagger}$ cannot be larger than the reactant entropy of melting, and $\exp(\Delta S^{\ddagger}/k)$ comes out normally between unity and 10^4. Occasionally $\exp(\Delta S^{\ddagger}/k)$ is found to be less than unity, as is the steric factor in gas reactions. Such a negative value of $\Delta S^{\ddagger}$ means that the activated complex is more ordered than the reactant (e.g. [21]). Experiments on some decomposition reactions have given K which are abnormally high in comparison to the theoretical values of (3). Hypotheses put forward to explain such discrepancies include co-operative activation [22], proton-delocalization [23], and a mobile layer of molecules on the reactant surface [18].

Kinetic analysis

Current practice

In determining the kinetics one wishes to find K_∞, E, and $f(1 - \alpha)$ or equivalently $F(\alpha)$ so that the reaction velocity can be predicted at any given T and α. This is commonly done by analyzing a set of $\alpha(t)$ or equivalently $\dot{\alpha}(t)$ values obtained by monitoring a number of samples reacting isothermally at a number of temperatures. The consistency of the K_∞ and E values with $f(1 - \alpha)$ should as far as possible be assessed, and correlated with, for instance, microscopy.

A quick method of calculating E was used by Haynes and Young [24]. Consider a set of (α, t) curves which have been found to be isomorphic. For any two curves (α_1, t_1) and (α_2, t_2) corresponding to temperatures T_1 and T_2 respectively, one can write

$$\begin{aligned} F(\alpha_1) &= t_1 K_\infty \exp(-E/kT_1) \\ F(\alpha_2) &= t_2 K_\infty \exp(-E/kT_2) . \end{aligned} \tag{5}$$

By choosing points corresponding to the same α on the two curves so that $F(\alpha_1) = F(\alpha_2)$, E can be evaluated by plotting ln t *vs.* $1/T$. On the other hand, to determine $F(\alpha)$ often a trial-and-error method is resorted to. Conflicting forms of the function have sometimes been asserted by several authors for the same material, like NH_4ClO_4 (see [25]) and KM_nO_4 (see [26]).

A conventional way of superimposing isothermal curves is to convert them into 'reduced-time plots' by individually scaling their t-axis with the factor $1/\tau_i$, where τ_i is the time when $\alpha = 0.5$ on the i-th curve. In this way $K(T_i)$ is absorbed into each scale factor and all $(\alpha, t) = (0.5, 1)$ points coalesce, while other $\alpha(t)$ points may be plotted out to see if the curves are indeed isomorphic. Sharp et al. [27] tabulate the theoretical values of α against t/τ for some of the $F(\alpha)$ shown in Table 1. They propose that by comparing experimental data with such master values the correct $F(\alpha)$ can be identified.

The above method may, however, result in ambiguity due to a number of aspects. Experimental data contain random errors, but no simple statistical analysis can be applied to the identification criterion it employs because no straight-line graphs are involved. Additionally, a general problem for all isothermal experiments is the zero-time uncertainty. The finite time taken by the sample to reach the designated temperature may be negligible relative to τ, yet may affect the comparison with the tabulated values [28]. Moreover, $F(\alpha)$ may change in different regimes of the $\alpha(t)$ curves, as mentioned earlier.

A new method

Here we suggest a step-by-step approach to determine $F(\alpha)$. It was noted by Hancock and Sharp [28] that for many forms of $F(\alpha)$, the plot of $\log[-\ln(1 - \alpha)]$ *vs.* $\log t$ is almost linear if α is restricted to between 0.15 and 0.5. Using a computer program to generate artificial values and their log-ln plots, we have found this true for all the theoretical forms listed in Table 1, with the exception of B, C and E. The slope in each case is listed there under the Column 'm'.

Obviously a log-ln plot is not very sensitive. If we were to rely solely on it to discriminate between the functional forms of $F(\alpha)$, the experimental data would have to be of the highest quality. A slightly more sensitive way is to plot $[-\ln(1 - \alpha)]^{1/m}$ *vs.* t, but then m can only be obtained iteratively. Fortunately, m does differ significantly between different groups of $F(\alpha)$, and the final discrimination is easily achieved by a further graphical step. There are three possible situations for this second step: –

1. $m \geq 2$ or log-ln concave upwards

It will be seen from Table 1 that this situation suggests an autocatalytic reaction, for which $\dot{\alpha} = K\alpha^p(1 - \alpha)^q$ for certain p and q. From the experimental data of $\dot{\alpha}$ and α, one can then do a least-squares fit on the graph of $\Delta \log \dot{\alpha}/\Delta \log \alpha$ against $\Delta \log(1 - \alpha)/\Delta \log \alpha$, and find p from the y-intercept and q from the slope. Here $\Delta \log \dot{\alpha} \equiv \log \dot{\alpha}(t_1) - \log \dot{\alpha}(t_2)$, etc.

For an $\dot{\alpha}$ expression of this form, one has $p(1 - \alpha') = q\alpha'$, where α' is the value at maximum $\dot{\alpha}$. Using this relation to reduce the number of unknown parameters to one, one can use a simpler graph to determine p and q [26]. However, the calculated values of p and q are then subject to the accuracy of α' and, more fundamentally, the possibility that p and q may change from one range of α to another is not allowed for. As mentioned above, those types of $f(1 - \alpha)$ in which $q = 0$ represent the acceleratory period which, in general should be followed by a decay period governed by a different form of $f(1 - \alpha)$.

2. $m \simeq 1$

The reaction is either phase-boundary controlled or unimolecular, and $\dot{\alpha} = K(1 - \alpha)^s$, as seen in Table 1. One then draws the graph of log $\dot{\alpha}$ against log $(1 - \alpha)$ to find r, the apparent reaction order.

3. $m \simeq 0.5$

The reaction is diffusion controlled (see Table 1). One has to test separately whether $\alpha(t)$ is parabolic (the diffusion is in one dimension), or $-\dot{\alpha}\ln(1 - \alpha) = K(1 - \alpha)^s$ with $s = 0$ (two dimensions) or $s = 1/3$ (three dimensions).

The correlation coefficient in the least-squares fit serves, by measuring the linearity of the $\dot{\alpha}$ graph, as a quantitative indication of the confidence to be attached to the identified form of $f(1 - \alpha)$. It may be that p and q, r, or s change once or twice as the reaction proceeds from beginning to completion, but the $\dot{\alpha}$ graphs will show it by displaying several linear segments. If however, a part of the graph say from (α_1, t_1) to (α_2, t_2) is non-linear, then $F(\alpha)$ has changed to a form in another group. The first step should then be repeated for that part: $\log\left[-\ln(1 - [\alpha + \alpha_1]/[1 - \alpha_1])\right]$ is plotted *vs.* $\log(t - t_1)$ for α between $\alpha_1 + 0.15(\alpha_2 - \alpha_1)$ and $\alpha_1 + 0.5(\alpha_2 - \alpha_1)$, followed by one of the above three alternative procedures. On the other hand, if a good fit is found with values of p and q, r, or s that are not in Table 1, the experimenter should assess whether theoretical justification can be provided. In this way new rate laws may be identified.

Confirmation is carried out by plotting the selected functional form or forms on top of the experimental curve. A slight misfit in the very early part (~ 1 minute, depending on the sample size and the environment) may be attributed to thermal lag-time and ignored. The $\dot{\alpha}$ graphs give K, and from a set of K values at different temperatures K_∞ and E can be determined. Note that the determination of these macro-kinetic constants depends on the form of $f(1 - \alpha)$ chosen, as it should be.

It may be added that we see it an immediate possibility to have full automation in the acquisition and processing of data in thermal analysis experiments. The hardware can be under the control of microprocessors or dedicated minicomputers, and their output would go into a computer or the same minicomputer. A computer program can then reduce the data to $\alpha(t)$ or $\dot{\alpha}(t)$ curves, and further analyse

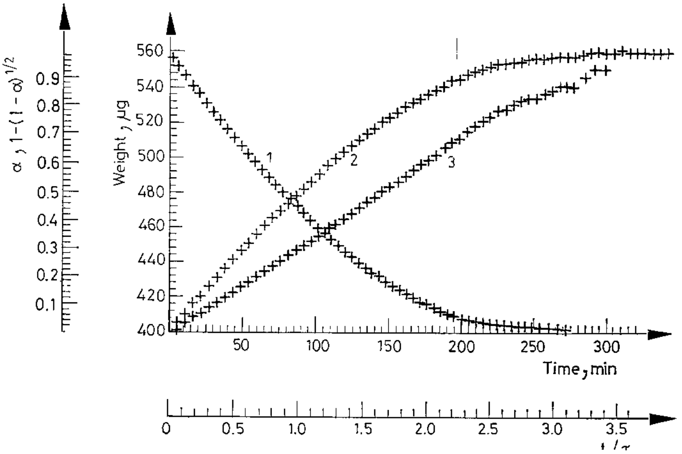

Fig. 1. Decomposition of a single crystal of AgN_3 at 551 K; 1. Thermogravimetric data, 2. α-time curve, 3. $1 - (1 - \alpha)^{1/2}$ *vs.* time.

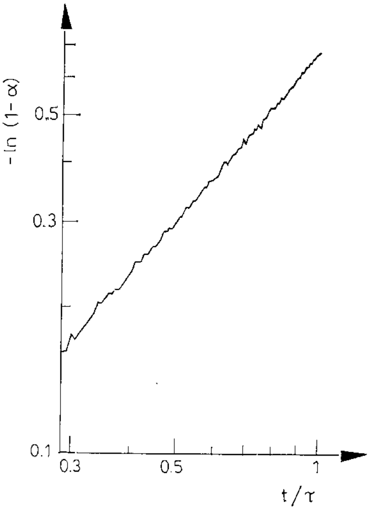

Fig. 2. Log-ln plot

the curves to identify $f(1 - \alpha)$ and so calculate K_∞ and E, according to the method proposed here. Nevertheless, the physical interpretation of these results by the experimenter remains the crucial step.

The method has been applied to investigate the kinetics of slow thermal decomposition in silver azide single crystals using thermogravimetric data. Curve 1 in Fig. 1 is a typical experimental curve of weight loss against time t, and Curve 2 is the corresponding reduced-time plot of α *vs.* t/τ. In Fig. 2 we plot log[$-$ln(1 $-$

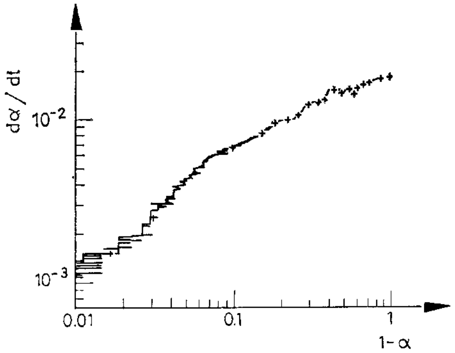

Fig. 3. $\dot{\alpha}$ graph

$- \alpha)]$ *vs.* $\log(t/\tau)$ for $0.15 < \alpha < 0.5$, obtaining essentially a linear graph of slope ≈ 1.1. The decomposition of AgN_3 therefore appears to be phase-boundary controlled or unimolecular. Accordingly, we draw in Fig. 3 the graph of $\log \dot{\alpha}$ *vs.* $\log(1 - \alpha)$. It shows that between $1 - \alpha = 1$ to 0.1, $\dot{\alpha} = K(1 - \alpha)^{\frac{1}{2}}$ with the correlation coefficient among the data points better than $+0.9$. Indeed, the plot of $1 - (1 - \alpha)^{\frac{1}{2}}$ *vs.* t (Curve 3, Fig. 1) is a good straight line, with a correlation coefficient of $+0.99$ for $0.1 < \alpha < 0.9$. The decomposition is thus of the contracting cylinder type. We have also obtained K_∞ and E, and found that their interpretation in terms of Eqs (3) and (4) leads to a plausible physical picture. Further details are given in a separate paper devoted to the mechanism of the thermal decomposition of AgN_3 [30].

In a second paper [29], we discuss the analysis of dynamic kinetic data which are easily obtained from modern thermoanalytical instruments.

Conclusion

We have described a systematic method for determining the kinetics of solid-state reactions from isothermal data. It may be stressed once more that whenever possible a judgement should then be made on the consistency of the K_∞ and E values with the implication of $f(1 - \alpha)$ regarding the likely mechanism of the reaction.

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References

1. D. A. YOUNG, Decomposition of Solids, Pergamon, Oxford, 1966.
2. J. SAWKILL, Proc. Roy. Soc. London, Ser. A 229 (1955) 135.
3. P. W. M. JACOBS and F. C. TOMPKINS, ibid., Ser. A 215 (1952) 265.
4. V. T. ROZENBAND and E. A. MAKAROVA, Combustion Expl. Shock Waves, 12 (1977) 601.
5. A. K. GALWAY and P. W. M. JACOBS, Proc. Roy. Soc. London, Ser. A 254 (1960) 455.
6. W. E. GARNER and L. W. REES, Trans. Faraday Soc., 50 (1954) 254.
7. H. R. HAILES, ibid., 29 (1933) 544.
8. E. G. PROUT and F. C. TOMPKINS, ibid., 40 (1944) 488.
9. M. J. AVRAMI, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
10. B. V. EROFEEV, Compt. Rend. Acad. Sci. U.S.S.R., 52 (1946) 511.
11. P. W. M. JACOBS and A. R. T. KUREISHY, Trans. Faraday Soc., 58 (1962) 551.
12. S. ROGINSKY and E. SCHULZ, Z. Phys. Chem., A138 (1928) 21.
13. J. Y. MACDONALD and C. N. HINSHELWOOD, J. Chem. Soc., 127 (1925) 2764.
14. J. B. HOLD, I. B. CUTLER and M. E. WADSWORTH, J. Am. Ceram. Soc., 45 (1962) 133.
15. W. JANDER, Z. Anorg. Allgem. Chem., 163 (1927) 1.
16. A. M. GINSTLING and B. I. BROUNSHTEIN, J. Appl. Chem. U.S.S.R., 23 (1950) 1327.
17. R. A. W. HILL, Trans. Faraday Soc., 54 (1958) 685.
18. R. D. SHANNON, ibid., 60 (1964) 1902.
19. W. NERNST, Z. Physik. Chem., 47 (1904) 52.
20. F. N. CAGLE and H. EYRING, J. Phys. Chem., 57 (1953) 942.
21. K. J. D. MACKENZIE and R. K. BANERJEE, Trans. J. Brit. Ceram. Soc., 77 (1978) 88.
22. W. E. GARNER, Nature, 144 (1939) 287.
23. J. J. FRIPAIT and F. TOUSSAINT, J. Phys. Chem., 67 (1963) 30.
24. R. M. HAYNES and D. A. YOUNG, Disc. Faraday Soc., 31 (1961) 229.
25. J. N. MAYCOCK and V. R. PAI VERNEKER, Proc. Roy. Soc. London, Ser. A 307 (1968) 303.
26. W. L. NG, Aust. J. Chem., 18 (1975) 1169.
27. J. H. SHARP, C. W. BRINDLEY and B. N. NARAHARI ACHAR, J. Am. Ceram. Soc., 49 (1966) 379.
28. J. D. HANCOCK and J. H. SHARP, ibid., 55 (1972) 74.
29. T. B. TANG and M. M. CHAUDHRI, submitted.
30. T. B. TANG and M. M. CHAUDHRI, Proc. Roy. Soc. London, Ser. A 369 (1979) 83.

RÉSUMÉ — Pour la plupart des réactions en phase solide, la vitesse de la réaction peut être décrite comme le produit de deux fonctions $K(T)$ et $f(1-\alpha)$, où T est la température et α le degré de conversion du solide en réaction. On discute l'interprétation de ces fonctions et on décrit une méthode systématique par laquelle on identifie $f(1-\alpha)$ d'une réaction à partir de ses données cinétiques. $K(T)$ et le mécanisme de la réaction sont déterminés ensuite. On a appliqué cette méthode avec succès à l'analyse de la cinétique de la décomposition thermique de l'azoture d'argent.

ZUSAMMENFASSUNG — Bei den meisten Festphasenreaktionen kann die Reaktionsgeschwindigkeit als Produkt zweier Funktionen, $K(T)$ und $f(1-\alpha)$ beschrieben werden, wobei T die Temperatur und α den Konversionsgrad des festen Reaktionspartners bedeuten. Die physikalische Deutung dieser Funktionen wird diskutiert und eine systematische Methode beschrieben, durch welche $f(1-\alpha)$ einer aus ihren kinetischen Angaben bestimmt werden kann. Danach werden $K(T)$ und der Reaktionsmechanismus bestimmt. Diese Methode wurde mit Erfolg zur Analyse der Kinetik der thermischen Zersetzung von Silberazid eingesetzt.

Резюме — Для большинства твердотельных реакций скорость реакции может быть описана как произведение двух функций $K(T)$ и $f(1-\alpha)$, где T — температура, α — степень превращения твердого реагента. Обсуждена физическая интерпретация этих функций и описан систематический метод, с помощью которого функция $f(1-\alpha)$ реакции может быть установлена из ее кинетических данных. После этого может быть определена функция $K(T)$ и реакционный механизм. Метод был успешно использован для анализа кинетики термического разложения азида серебра.