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ANALYSIS OF DYNAMIC KINETIC DATA FROM SOLID-STATE REACTIONS

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The kinetics of heterogeneous reactions, involving one reactant in the solid phase, usually follow the law $\dot{\alpha} = K_\infty \exp(-E/kT)f(1 - \alpha)$, where α is the degree of conversion of the solid, and K_∞ and E are the kinetic constants. A critical examination is given of the various methods which are currently used to analyse dynamic experimental data. The limitations of these methods and their insensitivity to the form of $f(1 - \alpha)$ are pointed out. An alternative approach free from these limitations is suggested. In this, $f(1 - \alpha)$ is determined from isothermal experiments, and then the dynamic data are accurately analyzed to obtain the values of the kinetic constants. A case study is given to elucidate the applicability of the approach.

There are many reactions of interest in which one of the reactants is in the solid phase. These reactions can be classified variously as decomposition, dehydration, calcination, dehydroxylation, reduction, polymeric inversion and degradation, oxidation etc., and they occur in a wide range of substances including ceramics, explosives and biological materials. The dynamic method of studying their kinetics involves measuring the reaction rates under conditions of a continuous temperature change.

Originally proposed by Skramovsky [1], the dynamic method is becoming increasingly popular, especially with the development of differential thermoanalytical techniques like DSC and DTA. Since the initial temperature can be chosen so that the reaction rate is relatively insignificant to begin with, it does not suffer from zero-time inaccuracy – a problem which exists in isothermal experiments where the temperature is raised rapidly and then held constant at a particular value. A further advantage is that, provided the dynamic data have been unambiguously and correctly analyzed, any changes in the kinetic constants will not be over-looked even within small temperature intervals. In contrast, the isothermal method only provides values averaged over discrete points in temperature. Also, when the method of analysis used is such that the kinetic constants are calculated from each dynamic curve then very few samples are required; only a milligram or so of the material is needed for its thermal characterization. If many runs are indeed carried out, differences between individual samples can be determined. The last two advantages are particularly useful in single crystal work.

On the other hand, intrinsic differences should be carefully distinguished from the effects of experimental conditions. In the first case literature data have shown that experimental parameters such as sample mass [53] and shape, particle size in the case of powder samples, and ambient atmosphere (or vacuum) can affect significantly the calculated values of kinetic constants (see [2]). If this happens, then whenever possible the empirical results should be extrapolated to refer to a 'standard' set of experimental conditions. Secondly, the heating rate very often affects the shape of the dynamic curve obtained, but discussion will be deferred to the next section. Lastly, the very fact that temperature is now a variable, in addition to time, complicates the analysis of data. If due care is not taken, either inaccurate or totally misleading values are obtained. In fact, a survey of the literature reveals several instances of high-quality experimental data being mis-interpreted by methods beyond their ranges of validity. In this paper, we first describe the various methods and point out their limitations. We then defend the approach in which use is made of both isothermal and dynamic experiments. The analysis of isothermal data yields $f(1-\alpha)$ (as defined below) unambiguously and, knowing $f(1-\alpha)$, one can calculate individual values of the kinetic constants from each set of dynamic data. We may mention that, historically, isothermal experiments were the only ones employed in the pioneering age in the twenties and thirties, when solid-state reactions began to be studied from the modern point of view, as distinct from that of Langmuir, Nernst and Tammann.

Kinetic equation

As discussed elsewhere [3] the kinetics of a reaction proceeding isothermally can usually be described by the empirical relation:

$$(\dot{\alpha})_{\text{isothermal}} = K_{\infty} f(1-\alpha) \exp(-E/kT). \tag{1}$$

Here α is the fraction of the solid reacted, k Boltzmann's constant, T the temperature, and $f(1-\alpha)$ and the constants K_{∞} and E are characteristic to the reaction. The function $f(1-\alpha)$ may change in different ranges of α but is, for a given α, independent of T, at least within a range of T. K_{∞} and E should be the same for the same $f(1-\alpha)$. If the rate-controlling step of the reaction occurs on the reactant-free surface or on the reactant-product (solid) interface, then K_{∞} will contain the surface-to-volume ratio. In other words, the reacting system should really be normalized per unit area rather than per unit size, and K_{∞} be given in units such as molecules $s^{-1} m^{-2}$.

Some authors have questioned the general validity of (1) on various grounds [4–7]. However, in the literature (1) is almost always successfully fitted to experimental data. Indeed, this empirical relation can be given mechanismic jutification (see [3]).

In dynamic experiments, also, it is commonly agreed that (1) may be adapted to describe the reaction rate:

$$\dot{\alpha} = K_{\infty} f(1-\alpha) \exp[-E/kT(t)] \tag{2}$$

$T(t)$ is controllable by the experimenter. Some temperature programs offer the mathematical advantage that $\exp[-E/kT]/\dot{T}$ can be integrated analytically (see later discussion on integral methods of data analysis). Examples are the hyperbolic program where $1/T = A - Bt$, i.e. $\dot{T} = BT^2$ [8, 9]; a parabolic program in which $AT^2 + BT - C = t$, i.e. $1/\dot{T} = 2AT + B$, with $B = AE/K_\infty$ by iteration [10]; and an exponential program so that $\dot{T} = \exp(-B/T)$ with $B \simeq E/k$ [10]. For the sake of experimental convenience, however, the arrangement is usually that $\dot{T} = \phi$ (A, C and ϕ represent constants in a particular run of experiment).

However, it has been taken by some authors who object to (2), that

$$d\alpha = \left(\frac{\partial\alpha}{\partial t}\right) dt + \left(\frac{\partial\alpha}{\partial T}\right) dT + \left(\frac{\partial\alpha}{\partial\phi}\right) d\phi \tag{3}$$

where $\left(\frac{\partial\alpha}{\partial t}\right)_{T,\phi} \equiv (\dot{\alpha})_{\text{isothermal}}$. The argument is then that (2) is seen to be inadequate even in the case of $d\phi = 0$, since the second term on the R.H.S. of (3) is nonzero but left out in (2): see e.g. [11, 12]. It has further been proposed [13], by a derivation starting from (3), that (2) is correct only if it includes the extra factor

$$[1 + (1 - T_0/T)E/kT]$$

in which $T_0 \equiv T(0)$. But we hold that (3) is unsound. Given t, T and ϕ, α is not uniquely determined and therefore not a function of these system variables; $\Phi d\alpha >> 0$, as α cannot decrease even for negative dT and $d\phi$! Nevertheless, the inexact differential $d\alpha$ can be integrated, if the dynamic process can be treated as the limiting case of a series of time intervals, during which the reaction proceeds isothermally according to (1) but at the end of each of which T is altered, in a time so short that during it the sample is unchanged. Along this path P the result is easily obtained [14]:

$$\int_0^\alpha \frac{d\alpha}{f(1-\alpha)} = \int_P K dt = \frac{K_\infty}{\phi} \int_{T_0}^T \exp(-E/kT) dT \tag{4}$$

where $K = K_\infty \exp(-E/kT)$. We must emphasize that (4) is not logically self-evident, as is sometimes implied [14] or argued by mathematical operations based on the presumption that $\alpha = \alpha(T, t)$ [15]. Rather, it comes from the assumption that the reaction under study involves no slow processes, so that $\dot{\alpha}$ depends only on the present values of α and T ($\dot{\alpha}$ is a function of state), but not on the history of the reacting system (c.f. [16]). Only by this assumption (absence of memory effects) can the dynamic process be treated as P. (Experimentally, a temperature program with temperature jumps, which approximates P, has been realized on a thermobalance interactively controlled by computer [17].) Equations (2) and (4) are of course equivalent. Their validity has also been shown by 'rational' thermodynamic arguments, in which the functional relation $\dot{\alpha} = g(t, \dot{K}t)$ is regarded as the 'constitutive equation' characterizing the reaction system [18]. In a new direction, the possibility has been suggested [64] that solid-state reactions may be studied by far from equilibrium thermodinamics.

On the other hand, experience shows that apparently (4) is not always followed exactly. Consider a reaction being investigated by a series of experiments conducted at different heating rates ϕ but with the same initial temperature T_0. In (4) we see that the R.H.S., for a given upper temperature limit T, is directly proportional to $1/\phi$. Plots of the L.H.S. *vs.* T should therefore all have the same shape. It may happen, however, that increasing departure from isomorphism is seen when experimental data obtained at higher ϕ are so analyzed. The most probable explanation is that the temperature change is too fast, causing the temperature distribution in the sample to become significantly non-uniform. In fact, thermal equilibrium is an underlying assumption when (4) is derived above; without it $\dot{\alpha}$ will depend on the thermal history of the reacting system.

Other factors may also be at work. The reaction rate may be sensitive to the structure of the reactant, and a higher ϕ can enhance the defect density or change the activation energy of reaction at a defect site [19]. In branched-chain reactions, the speed of the progressive accumulation of active centres may vary with the rate of change in temperature [20]. If the reaction is a surface process, the distribution of reaction 'centres' among corners, edges or faces of the sample may change with ϕ [21]. It may also be that the chemical system under study has multiple reactions proceeding concurrently in it, and they have different E [22]. All these variations in E may be accompanied by changes of K_∞ in the same direction. Because of this coupling, a linear relation between E and $\log K_\infty$ is sometimes observed. Called the 'compensation effect', this phenomena does not necessarily mean, as was suggested [4], that the Arrhenius expression in the R.H.S. of (4) is invalid. In all these cases, by varying ϕ the experimenter can, in fact, gain additional insights into the mechanism of the reaction, or distinguish between the competitive reactions in the reacting systems (a situation usually, though not always, indicated by the presence of multiple peaks in the $\dot{\alpha}$ curves). This is possible if the method of data analysis employed is such that K_∞ and E are determined from a single $\dot{\alpha}$ or α curve, rather than from data at a number of heating rates. The method we suggest will be of this type.

It may also happen that in (2) $K_\infty \propto T$, so that it cannot be taken outside the integral sign in (4). Indeed, modifications have been suggested of some methods of data analysis (those that assume a reaction order for the reaction) to take this extra temperature dependence into consideration [23]. However, even when theoretically required, the correction may for practical purposes be ignored, unless E is small or temperatures used are very high ($\mathrm{d}\ln K/\mathrm{d}T = [E + kT]/kT^2$). Likewise, any slight temperature dependence of E can usually be neglected. Furthermore, irrespective of this or the above complications the form of $f(1-\alpha)$ in (2) and (4) is not affected. It should be the same as that in (1), on the basis that the dynamic process can be treated as the limiting case of a series of isothermal intervals, as already mentioned above.

Data analysis

Experimentally, $\dot{\alpha}$ or α is obtained by DSC, DTA, TG, DTG, quantitative IR spectroscopy or X-ray diffraction, dilatometry, or measurements of chemi-luminescence, ultrasonic attenuation, dielectric constant, viscoelasticity, thermal or electrical conductivities, or optical reflectivity when changes in these characteristics can be correlated with α. The oldest technique is thermomanometry, in which the pressure of an evolved gas is measured at constant volume, but its use has so far been more popular in isothermal experiments. Many methods of analyzing $\dot{\alpha}$ or α data have been proposed to calculate the kinetic constants E and K_∞ (for a critical review of the earlier work see [24]) and sometimes also $f(1-\alpha)$. Often they were originally formulated with reference to one particular instrumentation, but they may be made generally applicable to all techniques after quantities measured on DSC, DTA, TG instruments etc. are all interpreted in terms of α and $\dot{\alpha}$. On the other hand, their validity does depend on the particular reaction whose data are being analyzed. Their limitations in this respect form the subject of our discussion below. They will be examined in three groups: peak-temperature, integral and derivative methods, in this order. Sophisticated instrumentation systems are coming into use, that incorporate computers to establish baselines or other null settings, to carry out automatic data acquisition, and to let the experimenter interactively analyse the data (e.g. [25]). Such advances do not, however, remove the danger of uncritical choices of the method of data reduction.

Critical examination of current methods

Peak-temperature method

Kissinger [26] considers reactions of the type $f(1-\alpha) = (1-\alpha)^n$. Differentiating (2) with respect to t, and setting the resulting expression to zero, he obtains

$$\dot{\alpha}_m(E/k)(\phi/T_m^2) = \exp(-E/kT_m)n(1-\alpha_m)^{n-1}\dot{\alpha}_m \tag{5}$$

in which m signifies 'peak' quantities, at the point of maximum $\dot{\alpha}$ where $\ddot{\alpha} = 0$. He next assumes that $n(1-\alpha_m)^{n-1} \simeq 1$; therefore

$$\phi T_m^{-2} \propto \exp(-E/kT_m) \tag{6}$$

regardless of n, which itself may be calculated from the shape of the α (t) curve. E and k, on the other hand, are obtained by performing a series of experiments at different ϕ. An aspect, which we regard as an inefficiency, of Kissinger's method is that only one point on the curve is used although, in the case where multiple peaks occur signifying that different $f(1-\alpha)$ and E govern different sections of the curve, the method should still be applicable to each peak.

There is, however, an important limitation. The a priori condition that $f(1-\alpha) = (1-\alpha)^n$ is actually valid only in very special circumstances, namely when the rate-limiting step of the reaction is the inward movement at a constant speed of the reactant-product interface, where n is 0, $1/2$ or $2/3$ for one-, two-, or three-dimensional movement, respectively, or when the reaction is unimolecular so that $n = 1$. Even among these special cases, the other approximation that Kissinger uses is still conditional, since $n(1-\alpha_m)^{n-1} \equiv 1$ only for $n = 1$. When n is $\frac{1}{2}$ or $2/3$, this expression varies with α_m approximately as $\Delta\alpha_m\, n(1-n)/(1-\alpha_m)^{2-n} \geq 0.2\, \Delta\alpha_m$, where $\Delta\alpha_m$ is the variation in α_m itself. In the Appendix we show that α_m changes with ϕ in the general case. Hence, when an apparent reaction order exists and is $\frac{1}{2}$ or $2/3$, Kissinger's method can lead to a systematic deviation in (6) and thus generate a significant but hidden error in the calculated E and K_∞.

If no apparent reaction order exists, then it definitely should not be used, otherwise an approximately linear plot from (6) results in totally misleading values of the kinetic constants. An example is in the decomposition of benzenediazonium chloride: it derives from DTA data a value of E that is 40% lower than the nearly identical values, obtained by applying other methods of analysis to the data from DTA as well as other techniques [27]. Other examples are in the study of lithium aluminium hydride, where the Kissinger values are half of the isothermal result [28], in RDX where it is again 40% lower than all the values calculated by other methods [29], and in urea nitrate, where it is 30% lower [30].

Integral methods

The L.H.S. of (4) is a function of α only and will be denoted by $F(\alpha)$; the R.H.S. can for practical purposes be equated with $\int_0^T K/\phi \, \mathrm{d}T$, since in experiments T_0 will be such that reaction velocity is negligible below it, i.e. $T_0 \ll E/k$. In view of these considerations, many authors have proposed different methods of analysing $\alpha(T)$ data.

The temperature integral $\int_0^T \exp(-E/kT)\mathrm{d}T$ has no analytical solution. (In the unusual case of a hyperbolic, parabolic or exponential temperature program, on the other hand, $\exp(-E/kT)/\dot{T}$ is integrable.) The numerical values of the integral have been compiled but, being a function of both E and T, are not directly useful unless an iterative solution of (4) by trial-and-error is resorted to. Such an approach has been advocated by Zsakó [31] who considers in particular the cases of $f(1-\alpha) = (1-\alpha)^n$ with $n = 0$, $1/3$, $1/2$, $2/3$, 1 or 2, when $g(\alpha) \equiv \log \int_0^\alpha \frac{\mathrm{d}\alpha}{f(1-\alpha)}$ has simple analytical expressions, and by Šatava and Škvára, [32] who generalize the method slightly by tabulating the values of $g(\alpha)$, $0 < \alpha < 1$, for some other forms of $f(1-\alpha)$.

For more efficient approaches, approximations to the integral are necessary. Thus, taking the first two terms in an asymptotic ($u \equiv E/kT \to \infty$) series of $\int_\infty^u \exp(-\tau)\frac{\mathrm{d}\tau}{\tau^2}$ Coats and Redfern obtain the linearized relation [33]:

$$\ln\left(F(\alpha)T^{-2}\right) = A - E/k(T^{-1}) \tag{7}$$

where $A = \ln(K_\infty k/E\phi)(1-2kT/E)$ is 'sensibly constant' if the range of temperature ΔT is small. They further assume that $f(1-\alpha) = (1-\alpha)^n$, and so $F(\alpha)$ can be calculated at each (α,T). Plotting (7) for several values of α thus gives E and K_∞, making use of only one set of data corresponding to a single ϕ.

Several cautionary notes should again be made here. The assumption for $f(1-\alpha)$ has already been discussed. Similar to the case of Kissinger's method, results obtained may be wrong and misleading if this functional form is not independently determined beforehand. Thus, in a study on the dehydroxylation of kaolinite [34], straight lines over different ranges of (T^{-1}) are given by (7) for a whole series of values of n, namely, 0, 0.5, 0.667, a and 2. In particular, plots using $n = 1$ and $n = 2$ are almost equally 'good'.

Secondly, the accuracy of the asymptotic approximation is rather low. By comparing its values with tabulated values of the integral [31, 35, 36], we find its relative errors to be $\Delta I/I = 20\%$ at $u = 5$, 5% at $u = 10$, and 1.5% at $u = 20$. Thus, for example, if E is 1 eV, then for an accuracy of 98% the highest temperature reached in the experimental run should not be more than 600 K, a very low figure for most materials though it is higher for larger E. Additionally, expanding A into a power series shows that $\Delta A/A \simeq 2k\,\Delta T/E$, so that at say 2% inaccuracy the range of temperature, ΔT, from which (α, T) points are selected should be less than 100K (for E = 1 eV). The total possible deviations in the calculated E and K_∞ are, to first approximation, the sum of the $\Delta I/I$ and $\Delta A/A$. It certainly is unsatisfactory if they are large and yet nowhere mentioned in the calculation.

Other approximations to the temperature integral have been suggested by van Krevelen *et al.* [37] and by Horowitz and Metzger [38], who made use of certain asymptotic expansions in the vicinity of T_m, the temperature at peak reaction rate. Both have been shown [39] to be even less accurate than the Coats and Redfern approach, and so will be left out in our discussion.

Amongst the integral methods, the best is probably the one due to Ozawa, which requires data at different ϕ but, in it $f(1-\alpha)$ remains completely general. The approximation to the temperature integral is: –

$$\int_0^T \exp(-E/kT)\mathrm{d}T \simeq \frac{E}{k}\,10^{(-2.32-0.457\,E/kT)} \tag{8}$$

so that from (4)

$$\log\phi_1 + 0.457(E/k)/T_1 = \log\phi_2 + 0.457(E/k)T_2 \tag{9}$$

where T_1 and T_2 are taken at an arbitrary but identical value of α in the two curves corresponding to heating rates ϕ_1 and ϕ_2. Plotting $\log\phi$ *vs.* $1/T$ for selected values of α should therefore produce straight lines, the slopes of which give E [40].

Three comments are appropriate here. By comparing (8) with tabulated numerical values, we see that it is 7% out at $u = 10$ or $T = 1170$K, and 3% and less only for $T < 720$K (if E = 1 eV). These errors should be examined before Ozawa's method is applied. Secondly, the method has been modified [41] to read, in place of (9),

$$\Delta \ln \phi / \Delta T_m^{-1} = 0.457\, E/k \tag{10}$$

in which $\Delta \ln \phi \equiv \ln \phi_1 - \ln \phi_2$, etc., and m denotes, as before, peak quantities. This relation may be compared with (6) but in general it does not hold since, as shown in the Appendix, α_m varies with ϕ. Lastly, like Kissinger's method, E cannot be determined from data at a single ϕ, and in some cases this may be a disadvantage, as discussed before.

Derivative methods

The derivative methods offer an advantage over those described above in invoking no mathematical approximations. Unfortunately, they use $\dot{\alpha}$ data which, with present instrumentation, tend to be of lower quality whether they are obtained by numerically differentiating the α data or are direct experimental read-outs.

The most straightforward, but as it stands relatively inefficient, of the derivative methods is to write (2) as: –

$$\ln\left(\dot{\alpha}/f(1-\alpha)\right) = \ln \mathrm{K}_\infty - E/kT \tag{11}$$

and to substitute different of $f(1-\alpha)$ until a linear plot appears [42]. Later, we shall argue, however, that even this labor omnia vincit approach like all dynamic methods in general, cannot guarantee correct values of E and K_∞ (nor an unambiguous form of $f(1-\alpha)$ in this specific case), although the labour it involves may be undertaken by the computer.

The earliest derivative method is probably that of Borchardt and Daniels, originally formulated for homogeneous reactions in the liquid phase [43] but later extended to solid-state reactions [44] for which it is now frequently used. The method puts $f(1-\alpha) = (1-\alpha)^n$ into (11), with n given a guessed value, and if a linear plot results then E and K_∞ are obtained from it. Based on this method, Hauser and Field [45] have developed a computer procedure, in which plots are generated for a series of values of n incremented at discrete steps, and the 'best' one is then selected to yield E, K_∞, and n. An attraction of this method is that n can be readily selected by eye. Alternatively, since in this case

$$\Delta \ln \dot{\alpha}/\Delta \ln(1-\alpha) = -\left(E/k[\Delta T^{-1}/\Delta \ln(1-\alpha)]\right) + n \tag{12}$$

a plot of the L.H.S. *vs.* the quantity in the square brackets at once gives E from the slope and n as the y-intercept [47]. If constant $\Delta \ln \dot{\alpha}$, $\Delta \ln(1-\alpha)$, or ΔT^{-1} is selected, Eq. (12) can be further simplified [61]. We have emphasized previously the fallibility in presuming such a convenient form of $f(1-\alpha)$; Ozawa [47] has commented on the possibility that this procedure, and the integral method of Coats and Redfern, may give false values of E and K_∞. In addition, since (12) involves the ratios of differences, the quality of data called for is even higher than that demanded alone by the use of $\dot{\alpha}$; experimental data so plotted more often than not show very large scatter. The Rogers and Morris method [48] plots $\Delta \ln \alpha$ *vs.* T^{-1}, and can be seen to be the special case of $n = 0$ in (12). An example of the general danger that very linear plots may sometimes appear even if the applied method is not valid is given by Patel and Chaudhri. The Rogers and Morris method was used to analyze DSC data on lead azide, and a straight line results although the calculated E turns out to be 180% larger than the Ozawa value [49]. Conversely, the coincidence of values calculated by various methods need not prove that these methods are all applicable to the case in hand. A counter-example is provided by a DSC study on RDX [29], where the Rogers and Morris value agrees well with other values but the complex decomposition is beyond doubt far from the $n = 0$ type.

On the other hand, Dávid and Zelenyánszki [50] plot $\ln\left[\left(\frac{\mathrm{d}}{\mathrm{d}t}(1-\alpha)\right)/(1-\alpha)\right]$ against (T^{-1}); this amounts to assuming a 'reaction order' $n = 1$. It serves as yet another example of the futility of linear plots, for their method gives such plots for the decomposition of 'a wide range of materials' including calcium oxalate and polyethylene which, most likely, are not of first or any other 'order'.

Some of the integral and derivative methods described in the foregoing have been compared by testing their accuracies on synthesised DTA data (exact as well as with artificial random error) for one E value and temperature range, the reaction considered being of the type with a reaction order [51]. Among the methods not included there is that due to Friedmann [52]. It probably is the most general among the derivative methods. Like Ozawa's procedure, it makes no assumption about $f(1-\alpha)$, although it requires $\dot{\alpha}$ data which, furthermore, have to be at a number of ϕ. Once again, from (2) with $\mathrm{d}\alpha/\mathrm{d}T \equiv \alpha^T$:

$$\ln(\alpha^T\phi) = \ln\left(K_\infty f(1-\alpha)\right) - E/kT. \tag{13}$$

Since $K_\infty f(1-\alpha)$ is identical for the same value of α, taking α^T and the corresponding T from several ϕ one can determine E.

It is our contention that even Friedmann's method has one basic limitation which, more significantly, is shared by all dynamic methods described above. The point in question is that all of them have to presume the constancy of $f(1-\alpha)$ as the temperature is changed. However, since mechanisms of solid-state reactions are generally complicated, there is no general justification for this presumption, though it may be true for particular reactions within specific temperature ranges. An illustration is the case where parallel reaction paths exist, each with values of K_∞ and E such that a quantitative change of T will lead to a qualitative change in the dominating path. Another case is where the identification of the rate-limiting step depends on T. Methods have been proposed which, by the use of computers, try different forms of $f(1-\alpha)$ in analyzing the dynamic data [53–55]. However, the search is limited to functional forms which are already known.

More importantly, from our own experience with azides we have strong doubts as to the exactness in determining $f(1-\alpha)$ or even its constancy from dynamic data. Likewise, in a study on the dehydration of manganese formate [54] for instance, no unique form of $f(1-\alpha)$ and correspondingly no unique values of E are identified even over appropriately restricted ranges of α, the criterion used being minimum standard deviation in the Arrhenius plot. Further examples are the thermal dehydroxylations of kaolinite [34] and of magnesium hydroxide [56]. We suggest that, in dynamic experiments since data are collected under variable temperature conditions, the change due to $f(1-\alpha)$ is inherently masked by that due to $K(T)$. This pitfall is illustrated in the Figures. Figure 1a shows the graphs of $\alpha(T)$ and its derivative which are generated artifically according to the theoretical equation $\alpha^T = K_\infty$ exp $(-E/kT)$ throughout from $\alpha = 0$ to $\alpha = 1$. The values chosen for K_∞ and E are 10^8 and 1eV respectively. Let us now examine how the data generated according to this relation, which is of the type $\alpha = Kt$, will be fitted by different kinetic equations, one of them being the correct one. In Fig. 1b we plot against $10^3/T$ the natural logarithms of the following expressions: –

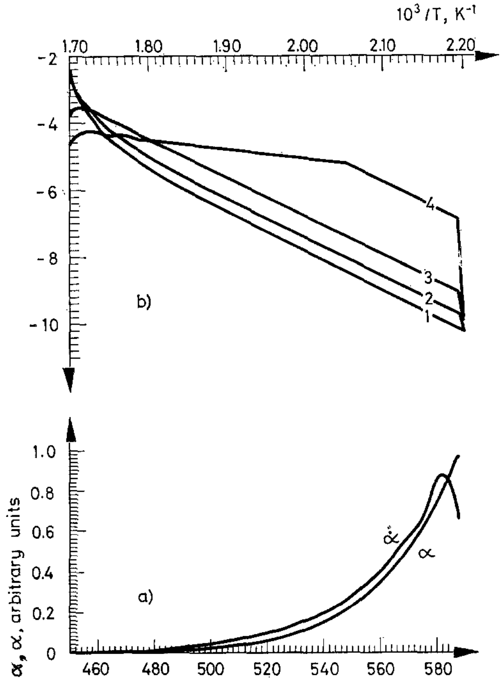

Fig. 1a. Artificial data $\alpha = Kt$, and corresponding $\alpha^T \equiv d\alpha/dT$ data, plotted against T which rises linearly with t

Fig. 1b. Arrhenius plots of: (1) $\alpha^T/3(1-\alpha)^{2/3}$, (2) $\alpha^T/2(1-\alpha)^{1/2}$, (3) α^T, and (4) $\alpha^T/3\alpha^{2/3}$ for the data shown in Fig. 1a

(1) $\alpha^T/3(1-\alpha)^{2/3}$, i.e. assuming $1-(1-\alpha)^{1/3} = Kt$: reaction controlled by three-dimensional contraction of phase boundary;

(2) $\alpha^T/2(1-\alpha)^{1/2}$, i.e. $1-(1-\alpha)^{1/2} = Kt$ type;

(3) α^T: the original assumption; and
(4) $\alpha^T/3\alpha^{2/3}$, i.e. $\alpha = (Kt)^3$: reaction controlled by e.g. three-dimensional growth of existing nuclei.

It is seen that the incorrect $f(1-\alpha)$ in (1) and (2) still give virtually linear plots, with slightly different slopes; interestingly, curve (4) is so misleading as to show two "linear" segments with a seemingly significant transition in between. Experimentally, Guarini *et al.* [57] have noted that it is impossible to ascertain from their DSC data whether the monomerization of 9-Me-10-AcAD has an apparent reaction order of 1, 0.67, or 0.5, in all of which cases E has about the same derived value.

The suggested approach

In the foregoing sections, we have discussed the limitations regarding the applicability of various methods that have been used to analyse dynamic data. In many published works we find that often a number of apparently different methods are used to analyse the same set of data. However, we think that in many cases this procedure is of no real significance, when some of the methods used are mathematically equivalent and therefore lead to the same results, or when some are invalid in the given situation and thus lead to doubtful values. The limitations of the methods express themselves both as discrepancies in the calculated values of the kinetic constants, and sometimes as fortuitous agreements when some of the methods are certainly inapplicable. (An extreme example of the second situation is that, for RDX, the Kissinger value [29] of E is near to that obtained [58] by plotting α *vs* T^{-1}, a procedure which has absolutely no theoretical justification.) Accordingly, we suggest that the interpretation of dynamic data should as far as possible be based on results from isothermal experiments. A similar approach has been used for studying the dehydroxylation of kaolinite by Achar, Brindley and Sharp [63].

One can unambiguously determine $f(1-\alpha)$ over the whole range of α and over the relevant temperature range, from the independent analysis of individual isothermal curves. A systematic method of efficiently implementing this identification has been proposed by us [3]. It may also be noted that thermoanalytical equipments are equally applicable in isothermal experiments (see e.g. [62]) though they are more often used in the dynamic mode. The identified form(*s*) of $f(1-\alpha)$ can then be substituted into either (2) or (4). In this way, form the dynamic α or $\dot{\alpha}$ data one can then determine accurately the non-average and single-sample values of E and K_∞: advantages which have been mentioned in the introduction to this paper. Moreover, the values will correspond individually to different heating rates.

We applied this approach to the spinel formation $ZnO + Cr_2O_3 \rightarrow ZnCr_2O_4$. A DTA curve (experimental atmosphere: N_2 at 300 mm mercury) was published in Ishii *et al.* [59], who have also monitored $\alpha(t)$ by chemical analysis when the reaction proceeded isothermally in nitrogen flowing at 50 ml/min, and showed that the isothermal data fit $[1 - (1-\alpha)^{1/3}]^2 = Kt$. We have measured K from the

Table 1

Isothermal data

T, deg. C	K relative units	$\ln K$
800	1	0
900	4	1.4
1000	23	3.1

Table 2

Dynamic data

T, deg. C	α	$\dot{\alpha}$ relative units	$\ln [x(x-1)\dot{\alpha}]$ $x \equiv (1-\alpha)^{-1/3}$
700	0.1	2	-2.6
820	0.15	4	-1.4
900	0.2	7	-0.54
1000	0.35	12	$+0.76$

experimental data points at $t = 20$ min in the published isothermal plots. From these values of K, given in Table 1, we calculate a value of 1.5 eV for E.

In Table 2 the values $\dot{\alpha}$ were measured from the published DTA curve whose heating rate was unspecified, and the α values were read off from the (α, T) graph which Ishii *et al.* have drawn presumably by integration. Now, from their analysis of the isothermal data the governing kinetic equation is, in differential form, $\dot{\alpha} = K/[(1-\alpha)^{-2/3} - (1-\alpha)^{-1/3}]$, at least within the ranges 800–1000° and α from 0 to $\simeq 0.6$ corresponding to $Kt = 0$ to $\simeq 0.07$. The Arrhenius plot of $\dot{\alpha}\,(1-\alpha)^{-1/3}$ $[(1-\alpha)^{-1/3} - 1]$, for the four data points shown in Table 2, is indeed a good straight line. From the plot we obtain $E = 1.3$ eV. In view of the probable experimental errors and inaccuracies in obtaining data from the published graphs, we consider satisfactory the reasonable agreement between this value and the one calculated from the isothermal data.

Conclusion

Most of the commonly used methods of analyzing dynamic data have been shown to be applicable only under particular conditions. It has been pointed out that to use these methods without considerations of the range of their validity can give misleading values of the kinetic parameters. An approach has been advocated in which use is made of both the dynamic and isothermal data; the functional form $f(1-\alpha)$ is determined from the isothermal experiments. This form in conjunction with the dynamic data, gives the values of the kinetic constants.

*

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Appendix

We wish to predict how the value of α at peak reaction rate varies with the heating rate ϕ. At $\alpha = \alpha_m$: from (4)

$$\int\limits_0^{\alpha_m} \frac{d\alpha}{f(1-\alpha)} - \frac{K_\infty}{\phi} \int\limits_{T_0}^{T_m} dT \exp(-E/kT) \equiv F(\alpha_m, \phi, T_m) = 0 \tag{14}$$

and from the fact that $\ddot{\alpha} = 0$

$$f'(1-\alpha_m) - \frac{E}{k} \frac{\phi}{T_m^2} \frac{\exp(E/kT_m)}{K_\infty} \equiv G(\alpha_m, \phi, T_m) = 0\,. \tag{15}$$

Solving the simultaneous equations $dF = 0$ and $dG = 0$, we find

$$\frac{d\alpha_m}{d\phi} = \left(\frac{\partial F}{\partial \phi}\frac{\partial G}{\partial T_m} - \frac{\partial F}{\partial T_m}\frac{\partial G}{\partial \phi}\right) \Bigg/ \left(\frac{\partial F}{\partial T_m}\frac{\partial G}{\partial \alpha_m} - \frac{\partial F}{\partial \alpha_m}\frac{\partial G}{\partial T_m}\right). \tag{16}$$

Defining dimensionless quantities $U = E/kT_m$, $\mu \equiv \phi/K_\infty T_m$, and $I(\alpha_m) \equiv \int\limits_0^{\alpha_m} d\alpha/f(1-\alpha)$, we have the following:

$$\frac{\partial F}{\partial \alpha_m} = \frac{1}{f(1-\alpha_m)}\,, \qquad \frac{\partial G}{\partial \alpha_m} = -f''(1-\alpha_m)\,,$$

$$\frac{\partial F}{\partial \phi} = \frac{K_\infty}{\phi^2} \int\limits_{T_0}^{T_m} dT \exp(-U) = \frac{I(\alpha_m)}{\phi}\,, \qquad \frac{\partial G}{\partial \phi} = \frac{\mu U}{\phi} \exp(U)\,,$$

$$\frac{\partial F}{\partial T_m} = \frac{1}{\mu \exp(U) T_m}\,, \qquad \frac{\partial G}{\partial T_m} = \frac{\mu U(2+U)}{T_m} \exp(U)\,. \tag{17}$$

Hence
$$\frac{d\alpha_m}{d\phi} = -\frac{U}{\phi} \frac{h(2+U)I(\alpha_m) - 1}{hU(2+U)/f(1-\alpha_m) - f''(1-\alpha_m)/h} \tag{18}$$

where $h \equiv \mu \exp(U)$. Incidentally, $dT_m/d\phi$ can be derived in a similar way.

The only case we find reported in the literature, in which α_m is apparently independent of ϕ, is the primary recrystallization of pre-compressed copper [60], where $\alpha_m \equiv 0.5$. In all other cases, experiments give changing α_m. We have made a rough check on (18) by taking the case of the decomposition of the explosive RDX [29], for which the Rogers and Morris method gives $E = 2.10$ eV and $K_\infty = 10^{18.4} s^{-1}$.

The reaction is complex, but these representative values are chosen because they correspond to an assumed kinetic equation in which $f(1-\alpha) = 1$. We thus have very simply $I(\alpha_m) = \alpha_m$ and $f''(1-\alpha_m) = 0$. For $\phi = 0.167$ K s^{-1}, α_m is given as 0.62 and T_m as 512K; our calculation shows $d\alpha_m/d\phi \simeq -0.1$ s K^{-1}, a value which compares well with the experimental indication that $\Delta\alpha_m/\Delta\phi = (0.60 - 0.62)/$ $/(0.333 - 0.167)$ s K^{-1}.

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Zusammenfassung — Die Kinetik heterogener Reaktionen mit einem Reaktionspartner in der Festphase folgt gewöhnlich dem Gesetz $\dot{\alpha} = K_\infty$ exp $(-E/kT)f/1-\alpha)$, wobei α der Konversionsgrad des Festkörpers sowie K_∞ und E die kinetischen Konstanten sind. Eine kritische Untersuchung der verschiedenen, laufend zur Analyse dynamischer Versuchsangaben angewandten Methoden wird gegeben. Die Grenzen dieser Methoden und ihre Unempfindlichkeit gegenüber der Formel $f/1-\alpha)$ werden aufgezeigt. Eine alternative Näherung, welche frei von diesen Beschränkungen ist, wird gegeben. Bei dieser wird $f(1-\alpha)$ aus isothermen Versuchen berechnet und nachfolgend die dynamischen Angaben genau analysiert, um die kinetischen Konstanten zu erhalten. Eine Fallstudie wird zur Erläuterung der Anwendbarkeit der Näherung gegeben.

Резюме — Кинетика гетерогенных реакций, включающих один реагент в твердой фазе, обычно подчиняется уравнению $\alpha = K_\infty$ exp $(-E/kT)f(1-\alpha)$, где α — степень превращения твердого тела, а K_∞ и E — кинетические константы. Представлено критическое исследование различных методов, обычно используемых для анализа динамических экспериментальных данных. Отмечены ограничения этих методов и их нечувствительность в отношение выражения $f(1-\alpha)$. Предложено альтернативное приближение, которое свободно от этих ограничений. В предложенном приближении член $f(1-\alpha)$ определяется из изотермических экспериментов, а затем динамические данные точно анализируются для получения значений кинетических констант. Представлен пример исследования с целью разъяснения применимости этого приближения.