

Note

**ANALYSIS OF ISOTHERMAL KINETIC DATA FROM MULTI-STAGE  
DECOMPOSITION OF SOLIDS**

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A decomposition in the solid state is a complex process which proceeds in many elementary steps. Irrespective of the details of the reaction mechanism, one of them will be the slowest under a given form of excitation (heat, ionising radiation, etc.) and within particular ranges of temperature,  $T$ , and molar fraction of decomposition,  $\alpha$ . This, as the rate-limiting step, will determine the reaction kinetics. To determine the kinetics, it is usual to monitor  $\alpha$  as a function of time,  $t$ , in a number of samples decomposed isothermally. The kinetic functions,  $f$  or  $F$ , and the rate constants,  $\kappa$ , are identified through the equation

$$\dot{\alpha} = \kappa_i(T) f_i(1 - \alpha) \quad (1)$$

or its integrated form

$$F_i(\alpha) = \kappa_i(T) t \quad (2)$$

the different  $\kappa$  and  $f$  or  $F$  being applicable to successive stages of the  $\alpha$ - $t$  curves. In this note, I wish to argue for certain precautions pertaining to this procedure. They may be overlooked if we do not always examine the physical, as contrasted with the formal, significant of  $F$  and  $\kappa$ .

Phenomenologically, a decomposition curve can, in general, be delineated into up to five sections: (1) initial rapid evolution of gas, (2) induction period, (3) acceleratory part, (4) deceleratory or decay period, and finally (5) retention [1]. In a specific reaction, one or more of sections 1, 2, 3 and 5 may be absent or so short as to be scarcely measureable. Obviously, an experimental curve showing only one section necessarily has its maximum  $\dot{\alpha}$  at  $\alpha = 0$ : it is deceleratory throughout its course [2]. Furthermore, experience shows that it will be either one- or two-stage. Indeed, considering the plausibility of deceleratory type mechanisms, I suggest that to fit any decay section with more than two functions,  $F$ , is inadmissible. On the other hand, if an induction period is found, an acceleratory and then a decay part invariably follow, although the latter two can occur without the former. These two parts may possibly fit one single  $F$ , as in the Avrami–Erofeev or in Prout–Tompkins equations, so that a sigmoid curve can be single-stage.

The physical interpretations of  $F$  help us to decide on alternative sequences of  $F$  proposed for a multi-stage reaction. For example, a

phase-boundary controlled type preceded by the linear law [2,3] or by an Avrami—Erofeev equation [3] is reasonable; one by the unimolecular decay law is not, since this law infers that each molecular unit on the surface or in the bulk possesses an equal probability for decomposition.

The analysis of the decay period, in the case when the F found for the acceleratory part does not apply, also requires a comment. Let the validity of this previous F end at the point  $(\alpha^*, t^*)$  on the isothermal decomposition curves; needless to say,  $\alpha^*$  has to be the same over a range of temperature for the fitting by F to be justifiable. Two different ways, both occasionally seen, of analysing the subsequent period is to try fitting its  $(\alpha, t)$  data to another F in the adjusted form

$$F(\alpha) = \kappa(T) t + [F(\alpha^*) - \kappa(T)t^*] \quad (3)$$

or in the form

$$F(\alpha - \alpha^*) = \kappa(T)(t - t^*) \quad (4)$$

In fact, neither form is satisfactory. There is a many-to-one correspondence between the forms of F and the topology of the phase boundary, but the onset of a new stage implies a topological change accompanied sometimes by a different rate-limiting step. Hence during this stage, the reacting system may be physically divided into two regions, one of which started to decompose only from  $t^*$  onwards and according to the new kinetic function, when the other had completely turned into the end product. The equation describing this stage should therefore be

$$F([\alpha - \alpha^*]/[1 - \alpha^*]) = \kappa(T)(t - t^*) \quad (5)$$

by a simple algebraic calculation to express the virtual fractional decomposition in terms of the overall fraction (or, equivalently, to convert the measured fraction into the "extended" fraction).

Equations (3)–(5) are not equivalent because F, being a deceleratory type, is necessarily non-linear (see Fig. 1). Admittedly, though, in practice both the correlation coefficient of the fit and the activation energy in  $\kappa$  may be little effected numerically, as many forms of F are virtually homogeneous functions of  $\alpha$ . We note, in contrast, that eqn. (3) may be used in the acceleratory part to allow for three effects. The effects are nuclear growth being dependent on size [4], time required by atoms to diffuse and then aggregate into nuclei [5], and coalescence of nucleus groups [6]. In the first two cases,  $t^*$  ought to be positive and in the last negative. Also, eqn. (4) may be used in the decay period when both the acceleratory and deceleratory parts are fitted by the Avrami—Erofeev equation, but the exponent of  $\kappa t$  after  $t^*$  becomes smaller. In this case, the topology of the reactant—product interphase has remained unchanged, although the decrease in the exponent implies the cessation of nucleation, only nuclear growth continuing.

It has to be emphasised that within each stage only one  $\kappa$  should be needed. An alteration in rate-limiting step is a sufficient (though, as mentioned before, not necessary) condition for a new F. Furthermore, there is, in general, a one-to-one correspondence between rate constants and elementary steps in any one reaction. Hence, a different  $\kappa$  can only appear in a new

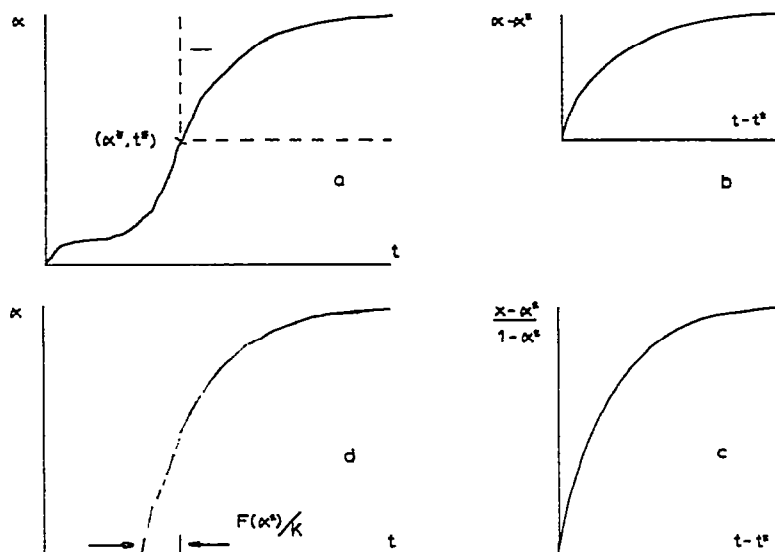


Fig. 1. The analysis of  $\alpha$ - $t$  data (a) from the decay period as a new stage: by plotting (b)  $F(\alpha - \alpha^*)$  vs.  $t - t^*$ , (c)  $F([\alpha - \alpha^*]/[1 - \alpha^*])$  vs.  $t - t^*$ , or (d)  $F(\alpha)$  vs.  $t$ . It is argued here that the correct way is (c).

stage. Any part of a decomposition curve which requires two  $\kappa$  for a fitted  $F$  (examples are shown in ref. 7 and quoted in ref. 3) ought, therefore, to be re-analysed with two  $F$ . Indeed, by way of contrast, the Avrami-Erofeev equation has a single  $\kappa$  for both the acceleratory and the decay sections: this  $\kappa$  is the product of the rate constants for nucleation and for growth with nuclear ingestion and overlap. In the Prout-Tompkins equation, the equality of  $\kappa$  for the two sections is in fact an underlying assumption; the equation is valid only if this condition is satisfied [1, p. 51]. It is usual, though not always, for the activation energy in  $\kappa$  to be smaller for later stages, or at most equal (as in barium styphnate monohydrate [8]). The major exception is that the rapid evolution of gas, when present as the first stage, can have the lowest activation energy. This activation energy is often a third of an eV or less when the underlying process is physi-desorption, although it will be between  $\approx 1$  and 2 eV in the case of chemi-desorption or true surface decomposition.

Lastly, a point concerning data manipulation. If the raw data reduce to  $\alpha(t)$  as in TG experiments and we have to calculate  $\dot{\alpha}(t)$ , experience suggests that this is best carried out by fitting the  $\alpha(t)$  curves, which are necessarily monotonic, with cubic splines and then differentiating analytically. When they are multi-stage, then to obtain a good fit we should, in the computer program, prescribe more closely spaced knots, and choose smaller smoothing parameters if specifiable in the subroutine used, for the transitional parts between stages.

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