Discussion

Comments on "Rigorous determination of kinetic parameters from DTA measurements"

A recent paper [1] described a method for calculating kinetic parameters from differential thermal analysis (DTA) curves, which was "rigorous" as no use was made of the so-called Piloyan's approximation and the assumption that the peak of an individual curve corresponded to a maximum reaction rate. The method is restricted to a process shown by former work to follow an Avrami–Erofeev type of kinetic equation, throughout the entire course of the reaction, and with an invariant index n. DTA thermograms at a number of constant heating rates h are required. The calculation involves the values of h, T_m and S_m, where $T_m \equiv T_m(h)$ are the peak temperatures and $S_m \equiv T_m - T_0$, T_0 being the starting temperature of the heating programmes.

Two comments are in order. The first point is that, with the form of the kinetic equation already known, several procedures (e.g. [2]) have been established by which kinetic parameters can be determined without recourse to nonlinear multiple regression analysis, in contrast to the proposed method. The latter does, nevertheless, offer an advantage in comparison since no evaluation of areas under the thermograms is necessary.

More crucially, however, there is a doubt regarding the appearance of S_m as input data to the calculation. The reason is that T_0 is arbitary in so far as the reaction rate coefficient k remains negligibly small at the start of the experiment. When any $T'_0 < T_0$ has been chosen instead the same T_m should be measured corresponding to a given h. A different $S'_m = T'_m - T'_0$ would accordingly be obtained, leading to results distinct in general from the original set. This situation clearly looks self inconsistent.

I suggest that the method needs a revision because the kinetic equation relating the fraction reacted to time t:

$$\alpha = 1 - \exp\left[-(kt)^n\right] \tag{1}$$

used in its derivation, is invalid except under isothermal conditions. This point has in fact been raised before in the journal, and was, in another form, the subject of a previous controversy (e.g. [3]). As it is now obvious that quite a few authors ([1, 4–7]) still disagree with the invalidity of Equation 1, a more detailed discussion may be helpful here.

The argument lies in the fact that α is not a thermodynamic state variable of the reactant: Equation 1 by itself has no significance on the basic level. On the other hand, k is such a variable, being a function solely of temperature (and pressure) as long as the activated complex of the reactant, i.e. the transition state in the reaction path, has a mean lifetime short relative to the time interval over which k increases appreciably due to the rising temperature. The basic equation describing the kinetics of the reaction is therefore:

$$\frac{d\alpha}{dt} = \left[-\ln(1-\alpha)\right]^{1-1/n}(1-\alpha)k \tag{2}$$

where on the right hand side the two factors containing α account for the evolving geometry of the reactant–product interface. On separation of variables and integration Equation 2 becomes:

$$\ln(1-\alpha) = -\left(\int_0^t k\,dt\right)^n. \tag{3}$$

Only in the special case when temperature and thus k are constant does the above reduce to Equation 1. Otherwise, α depends not on the instantaneous value of k and t but on the complete thermal history of the reacting system, and the original Equation 3 has to be used. Alternatively, the derivation of the method may start with Equation 2: the ensuing mathematics will probably be simpler.

References

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Reply to 'Comments on "Rigorous determination of kinetic parameters from DTA measurements"'

We are grateful to Dr Tang for his comments on our paper because it gives us a chance to clarify some perhaps obscure points which appeared in our work.

Firstly, we do not know of any other method which simultaneously allows the determination of all three kinetic parameters by means of differential thermal analysis (DTA). Ozawa [1] applied his method by using thermogravimetric (TG) equipment on reactions characterized by weight loss.

Concerning the arbitrary choice of T_0, which influences T_m and consequently the kinetic parameters, we agree with Tang when he states that at low temperatures the reaction rate is low. We must therefore expect that a lower T_0 would not change T_m values to a great extent. If we use, for simplicity, the expression $A = (h/S_m)\exp(\beta/T_m)$, by inserting $h = 10° \mathrm{C\,min^{-1}}$, $S_m = T_m - T_0$, $\beta = 27\,880\,\mathrm{K}$, $A = 6.64 \times 10^{11}\,\mathrm{sec^{-1}}$, $T_0 = 293.15\,\mathrm{K}$, $T_0' = 250\,\mathrm{K}$, $T_0'' = 200\,\mathrm{K}$, and resolving for T_m, we obtain respectively: $T_m = 829.7$, $T_m' = 827.9$, $T_m'' = 825.9\,\mathrm{K}$. This demonstrates that the contribution of the low temperature range is almost ineffective to the reaction rate that our expression accounts for this statement.

There is still deep controversy concerning the application of the Avrami–Erofe'ev rate equations to non-isothermal reactions. Most workers apply the so-called Avrami–Erofe'ev rate equation in dynamical conditions. On the other hand a few authors have explicitly used the integral Avrami–Erofe'ev equation in the same cases [2, 3]. We have followed these workers and think that it is significant that our experimental results are in excellent agreement with the more accepted isothermal data, at least in Li_2O–$2SiO_2$ glass devitrification.

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