Thermochimica Acta, 57 (1982) 93–98
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

ANALYSIS OF DYNAMIC KINETIC DATA FROM A SINGLE STAGE IN THE DECOMPOSITION OF SOLIDS

T.B. TANG

Physics and Chemistry of Solids, Cavendish Laboratory, Cambridge CB3 OHE (Gt Britain)

(Received 12 February 1982)

ABSTRACT

It is suggested that determining the kinetics of a solid-state decomposition requires at least two experiments. The kinetic function can be determined from an isothermal experiment and the rate constants from a dynamic experiment. A method is described by which the rate constants, namely activation energy and frequency factor, may be evaluated from the dynamic data if a single kinetic function applies throughout almost the entire course of the reaction. For special cases of the kinetic function, the rate constants can be simply calculated by noting the points of maximum positive and maximum negative slopes on the experimental curve of reaction.

There are many decomposition reactions of current interest, in which the reactant is in a solid phase. The rate of a reaction involving the solid state can almost always be expressed as

$$\frac{d\alpha}{dt} = A \exp(-E/kT) f(1-\alpha) \equiv K f(1-\alpha) \qquad (1)$$

where α is the molar fraction of the reactant which has decomposed by time t, A is the frequency factor, E is the activation energy, T is the temperature, and k is the Boltzmann constant. Often the kinetic function $f(1-\alpha)$ and the rate constants A and E remain unchanged throughout a major part of the course of a reaction. This note describes an alternative approach in measuring these parameters of such a reaction, requiring minimum experimental and numerical work. In contrast [1], the kinetic analysis of a multi-stage reaction is much more complicated, and sometimes gives unambiguous results only after the plausibility of alternative physical mechanisms for the reaction has been carefully evaluated.

Many methods have been proposed for kinetics determination by dynamic experiments, in which the reaction is made to proceed under a linearly rising T. Dynamic measurements to a high accuracy can easily be made with modern thermoanalytical instruments and do not suffer from the zero-time problem of isothermal experiments. However, $f(1-\alpha)$ cannot be reliably

0040-6031/82/0000-0000/$02.75

ascertained from dynamic data, and those methods for finding E and A which presume no knowledge of the kinetic function require data from many experiments performed at different $\phi \equiv dT/dt$ [2]. Even when $f(1-\alpha)$ is known, the analysis of data at one ϕ involves considerable numerical processing in any of the methods currently used [2].

It is suggested here that a minimum of two experiments are needed to determine $f(1-\alpha)$, A and E for the single stage of a reaction under investigation. A dynamic experiment is carried out, from which the 'onset' and 'completion' temperatures of the reaction at the chosen ϕ can be estimated. The second, isothermal run is then made at a temperature roughly half way between these two approximate values. As far as possible the two experiments should be performed under identical conditions, excepting of course the temperature. The isothermal data are used to confirm $f(1-\alpha)$ according to, for example, the log–ln method described in ref. 3. The dynamic data are then analyzed. A simple method is considered here which allows the convenient calculation of E and A from the dynamic experimental curve, representing $d\alpha/dT$ as is the case when DSC, DTG, DTA or any of the other differential instruments has been employed. In general, three points of special significance stand out on the curve namely, maximum positive slope, zero slope and maximum negative slope, giving rise to five identifiable temperatures T_1–T_5, as illustrated in Fig. 1. The 'onset' and 'completion' temperatures, T_0 and T_c, are also shown but their (finite) values

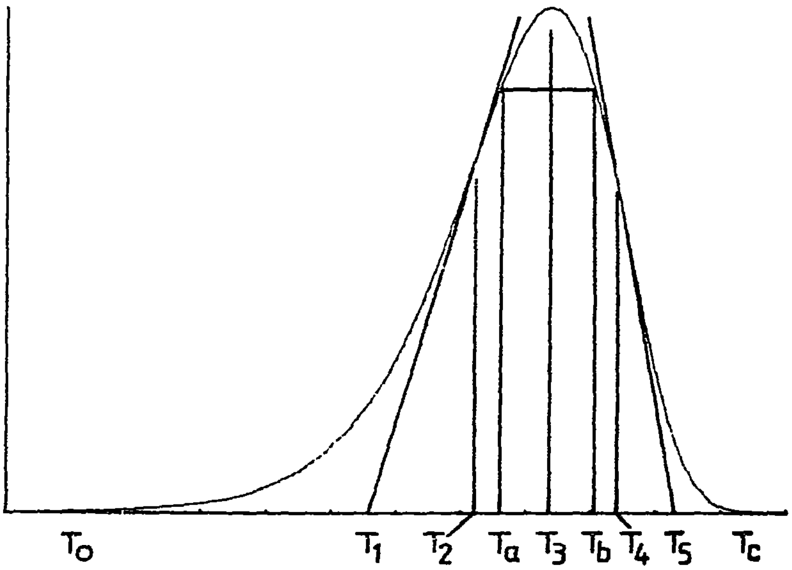

Fig. 1. Trace of reaction rate vs. temperature that increases linearly with time. Five temperature values, T_1–T_5, can be specified by the trace; the 'onset' and 'completion' temperatures, T_0 and T_c, respectively, are less well defined. T_a and T_b are any pair of temperatures at which the reaction rate is the same.

are really not sharply defined. The other five temperatures are given by

$$T_3\colon \frac{d^2\alpha}{dT^2}=0,\ \frac{d\alpha}{dT}\neq 0 \tag{2}$$

$$T_2,\ T_4\colon \frac{d^3\alpha}{dT^3}=0,\ \frac{d\alpha}{dT}\neq 0 \tag{3}$$

$$T_1,\ T_5\colon T_i-\left(\frac{d\alpha}{dT}\right)_{T_i}\Big/\left(\frac{d^2\alpha}{dT^2}\right)_{T_i},\ i=2 \text{ or } 4 \tag{4}$$

Now, among forms of $f(1-\alpha)$ commonly met, those that may apply to almost the entire course of a reaction are $(1-\alpha)^{1-1/n}$, $n=2$ or 3, and $(1-\alpha)\ [-\ln(1-\alpha)]^{1-1/n}$, $n=1,\ 2,\ 3,\ 4,\ \ldots$. Other usual forms imply constant or accelerating reaction rates, and are unlikely to remain valid beyond a short stage at the beginning of the reaction. Equation (1) may be rewritten as

$$\int_0^{\alpha}\frac{d\alpha}{f(1-\alpha)}=\int_0^{t}K\,dt\equiv I \tag{5}$$

which, for the two forms of $f(1-\alpha)$ stated above, becomes, respectively

$$\alpha=1-(1-I)^n \qquad n=2 \text{ or } 3 \tag{6}$$

$$\alpha=1-\exp(-I^n) \qquad n=1,2,\ldots \tag{7}$$

It is found here that, for certain cases of eqns. (6) and (7), E and A may be calculated very quickly from T_2 and T_4*. Unfortunately, the calculation in the other cases has to be slightly less direct, and no elegant relations between the rate constants and T_1, T_3 or T_5 have been uncovered. Consider eqn. (6). Successive differentiation gives

$$\frac{d\alpha}{dT}=n(1-I)^{n-1}\frac{K}{\phi} \tag{8}$$

$$\frac{d^2\alpha}{dT^2}=\frac{E}{kT^2}\frac{d\alpha}{dT}-\frac{n-1}{1-I}\frac{K}{\phi}\frac{d\alpha}{dT} \tag{9}$$

$$\frac{d^3\alpha}{dT^3}=\frac{E}{kT^2}\frac{d^2\alpha}{dT^2}-\frac{2E}{kT^3}\frac{d\alpha}{dT}-\frac{n-1}{1-I}\frac{K}{\phi}\frac{d^2\alpha}{dT^2}$$
$$+\frac{n-1}{(1-I)^2}\frac{K^2}{\phi^2}\frac{d\alpha}{dT}-\frac{n-1}{1-I}\frac{E}{kT^2}\frac{K}{\phi}\frac{d\alpha}{dT} \tag{10}$$

If eqn (9) is put into eqn. (10), and $-2E/(kT^3)$ is ignored compared with

---

* The evaluation of E from T_2 and T_4 was investigated in a recent paper [4]. However, the derivation there did not use the correct form of the kinetic equation [eqn. (5) here] and appears, therefore, to be erroneous.

$(E/kT)E/(kT^3)$—a simplification which is acceptable unless, exceptionally, the activation energy E is very low and correspondingly T in the experiment is high— then eqns. (3) reduce to

$$(n-1)(n-2)X^2 - 3(n-1)X + 1 = 0 \tag{11}$$

where $X \equiv (K/\phi)(kT^2/E)/(1-I)$.

When n is 2, only one solution exists—there is no point of maximum negative slope on the $\mathrm{d}\alpha/\mathrm{d}T$ curve. For the $n = 3$ case, however, expressing the ratio and then the product of the two solutions by the coefficients of the quadratic equation while making use of relation (8), finally gives

$$E = \tfrac{2}{3}k\left[\ln\frac{3+\sqrt{7}}{3-\sqrt{7}} - 2\ln\frac{T_4}{T_2} + \tfrac{1}{2}\ln\frac{(\mathrm{d}\alpha/\mathrm{d}T)_{T_4}}{(\mathrm{d}\alpha/\mathrm{d}T)_{T_2}}\right]\Big/\left(\frac{1}{T_2} - \frac{1}{T_4}\right) \tag{12}$$

$$A = \left(\frac{E^2}{6k^2T_2^2T_4^2}\right)^{1/3} \phi\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T_2}^{1/6}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T_4}^{1/6} \exp\frac{E}{2k}\left(\frac{1}{T_2} + \frac{1}{T_4}\right) \tag{13}$$

Note that in eqn. (12) only the relative heights of the curve at T_2 and T_4 are required and they can be read directly from the chart recording. In practice, the terms involving them as well as that in the middle of the square bracket are often small compared to the leading term. Hence, as a first estimate

$$E \approx \frac{15.4}{(1/T_2 - 1/T_4)}\ \mathrm{J\ mole^{-1}}\ \text{or}\ \frac{0.159}{(1/T_2 - 1/T_4)}\ \mathrm{meV} \tag{14}$$

where T_2 and T_4 are in Kelvin.

When $n = 2$, eqns. (6) and (8) lead to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{2A}{\phi}(1-\alpha)^{1/2}\exp(-E/kT) \tag{15}$$

Thus, by drawing any horizontal line to cut the experimental $\mathrm{d}\alpha/\mathrm{d}T$ curve at two points, corresponding to temperatures T_a and T_b, respectively, one gets

$$E = \tfrac{1}{2}k\ln\frac{1-\alpha_a}{1-\alpha_b}\Big/\left(\frac{1}{T_a} - \frac{1}{T_b}\right) \tag{16}$$

In this case, slightly more work is needed to find $\alpha_a \equiv \alpha(T_a)$ and α_b. The quickest way, experience suggests, is by photocopying the curve and cutting out the area under it. The area is weighted, as a whole, with the part outside the line at T_b removed, and then with that beyond T_a cut off. The appropriate ratios give α_b and α_a.

Let us now consider the kinetic type (7).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = nI^{n-1}\exp(-I^n)\frac{K}{\phi} \tag{17}$$

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}=\frac{\mathrm{d}\alpha}{\mathrm{d}T}\left\{\frac{E}{kT^2}+\left[(n-1)I^{-1}-nI^{n-1}\right]\frac{K}{\phi}\right\}\equiv\frac{\mathrm{d}\alpha}{\mathrm{d}T}\{S\} \tag{18}$$

$$\frac{\mathrm{d}^3\alpha}{\mathrm{d}T^3}=\frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}}{\mathrm{d}T}\{S\}+\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)^2\{S\} \tag{19}$$

and eqns. (3) eventually take the form

$$\begin{aligned}&[(n-1)(n-2)+3n(n-1)\ln(1-\alpha)+n^2\ln^2(1-\alpha)]Y^2+3[(n-1)\\&\qquad+n\ln(1-\alpha)]Y+1=0\end{aligned} \tag{20}$$

where $Y\equiv(K/\phi)(kT^2/E)/I$, and the last term on the left-hand side has been obtained again with the assumption that $E/kT\gg 2$. When n is 1, taking the ratio and then the product of the two roots of eqn. (20) we see that

$$E=k\left(\ln\frac{3+\sqrt{5}}{3-\sqrt{5}}-2\ln\frac{T_4}{T_2}\right)\bigg/\left(\frac{1}{T_2}-\frac{1}{T_4}\right) \tag{21}$$

$$A=\frac{E\phi}{kT_2T_4}\exp\frac{E}{2k}\left(\frac{1}{T_2}+\frac{1}{T_4}\right) \tag{22}$$

It may be necessary to emphasize that, after E has been calculated, the magnitude of E/kT_4 should be considered and the validity of the original assumption established. The same consideration applies to the use of eqn. (12), and usually the expression for E may again be simplified. Unless the heating rate adopted in the experiment has been very low, T_2 and T_4 are usually fairly close together, and if (say) $T_4-T_2\equiv\Delta T<0.1T_2$, then

$$2\ln(T_4/T_2)<0.191\ll\ln[(3+\sqrt{5})/(3-\sqrt{5})]=1.93$$

so that, to better than 10% accuracy

$$E\approx 0.166\frac{T_2}{1-1/(1+\Delta T/T_2)}\approx 0.166\frac{T_2^2}{\Delta T}\,\mathrm{meV} \tag{23}$$

where T_2 and ΔT are in Kelvin.

Unfortunately eqn. (20) cannot be solved for $n=2, 3, \ldots$. Proceeding as in the previous case, one gets

$$E=k\left[\ln\frac{1-\alpha_a}{1-\alpha_b}+\frac{n-1}{n}\ln\frac{\ln(1-\alpha_a)}{\ln(1-\alpha_b)}\right] \tag{24}$$

analogous to eqn. (16).

A test of eqn. (23) has been made on data obtained by computer simulation. The curve in Fig. 1 was generated by a computer programme according to

$$\frac{d\alpha}{dt} = K \exp\left(-\int_{300\ \mathrm{K}}^{T} K \frac{dT}{\phi}\right) \tag{25}$$

where ϕ was 1 K s^{-1}, $K = (10^{12}/s)\exp(-1.16 \times 10^4\ K/T)$, i.e. $E = 1$ eV, and T increased to 420 K. As measured from the graph, T_2 and T_4 are 372 and 394 K, respectively. (This can be accurately done by drawing the respective line of maximum slope, and taking the mid-point of that segment of it which really cannot be distinguished from the $d\alpha/dt$ curve.) Thus $\Delta T = 22\ K \ll T_2$, and eqn. (23) gives 1.05 eV, in good agreement with the original value.

In conclusion, an approach to kinetic analysis has been suggested which requires only two experimental runs to be performed. An isothermal experiment confirms the type of kinetic function, and rate constants are determined from dynamic data, for which calculation several formulae have been derived. In particular cases of kinetic functions given in eqns. (6) and (7), an approximate formula for the activation energy takes the form $E \approx 0.16\ T_2^2/\Delta T$ as in eqns. (14) and (23). The method may be of relevance to the situation when a rapid assessment of the thermal reactivities of various chemicals is required.

ACKNOWLEDGEMENTS

This work was supported by the Procurement Executive, Ministry of Defence, and by the award of the Charles and Katherine Darwin Research Fellowship from Darwin College, Cambridge. I thank Mr. S.J.P. Palmer for implementing the computer programme on a Hewlett-Packard 9825A calculator, and Drs. M.M. Chaudhri and J.E. Field for helpful comments.

REFERENCES

1 T.B. Tang, Thermochim. Acta, 41 (1980) 133
2 T.B. Tang and M.M. Chaudhri, J. Therm. Anal., 18 (1980) 247.
3 T.B. Tang and M.M. Chaudhri, J. Therm. Anal., 17 (1979) 359.
4 A. Marotta, S. Saiello, F. Branda and A. Buri, J. Mater. Sci., 17 (1982) 105.