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Rigorous determination of kinetic parameters from DTA measurements

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A rigorous analysis of the application of the DTA technique to the solid-state reaction formally described by the Avrami–Erofe'ev equation leads to a quantitative relationship among the experimental parameters obtainable from thermograms. A non-linear regression procedure allows the simultaneous evaluation in a very simple way of the activation energy, E_{act}, of the reaction order n and of the pre-exponential Arrhenius factor, A. The knowledge of these quantities leads to considerations about the reaction mechanism and to the complete prevision of the behaviour of the transformation. Isothermal literature data totally agree with our experimental results.

1. Introduction

The reaction rate of a solid-state transformation is expressed in a general way by:

$$\frac{d\alpha}{dt} = kf(\alpha), \tag{1}$$

where α is the fractional reaction, k the reaction-rate coefficient and t the time. Equation 1, if the analytical form of the $f(\alpha)$ function is known, can be integrated as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = kt.$$

It has been demonstrated that very large classes of solid-state reactions (decompositions, phase transformations, crystallizations) can be completely described by an "integral" rate equation, which is the so-called Avrami–Erofe'ev relationship [1–4]:

$$-\ln(1-\alpha) = (kt)^n. \tag{2}$$

In general, k depends on the absolute temperature in accordance with the Arrhenius equation:

$$k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right), \tag{3}$$

where A is the Arrhenius pre-exponential factor.

It is clear that a complete characterization of a generic solid-state reaction and then obviously also of a reaction following the Avrami–Erofe'ev equation is reached only if the numerical values of E_{act}, n and A are known.

In order to determine these kinetic parameters, the "isothermal analysis" is surely the most common procedure. In this perspective, it is necessary indeed to measure in some way (i.e. by means of X-ray diffraction, optical microscopy, isothermal differential calorimetry, etc.) many values of α as a function of t at a selected constant temperature. Then, it is possible to fit the Avrami–Erofe'ev equation at the fixed temperature and determine the values of k and n. By iterating this procedure, it is possible to obtain several values of k at different temperatures. An Arrhenius plot then allows the evaluation of A and E_{act}. Although very precise and accurate, this method needs very long and complicated experimental measurements and therefore it is not completely suitable.

On the other hand, the non-isothermal or dynamic methods, such as DTA, non-isothermal DSC, TG, supply a complete overview of the

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reaction trend by scanning the whole temperature range of interest in a continuous way. Nevertheless, the existing procedures of analysis of the experimental data (in particular those obtained from DTA) are all affected by some kind of serious approximations, or are unable to supply simultaneously all the kinetic parameters.

In this perspective, many papers since 1956 have appeared, concerning DTA kinetic analyses of the solid-state reactions. The first work on the evaluation of kinetic parameters was published by Kissinger [5, 6] and was based on a model different from the Avrami–Erofe'ev equation. This method was proved invalid on theoretical and experimental grounds in a later paper by Reed *et al.* [7], because of its incorrect assumption that the maximum reaction rate is reached exactly at the top of DTA peaks. In 1966, Piloyan *et al.* [8] enunciated the so-called "Piloyan's approximation", stating that in the initial part of the DTA peak the rise of temperature has a much larger influence on the temperature differential, ΔT, than on the fractional reaction, α. It is evident that this approximation may lead to many simplifications in the mathematical treatment of the DTA theory. On Piloyan's work were substantially based the kinetic methods of Šesták [9] and Marotta and co-workers [10, 11] which, on the basis of the Avrami–Erofe'ev equation, allowed the determination of E_{act} and n. Nevertheless, their procedure of application of the Piloyan's approximation was criticized by Criado and Ortega [12]. An approximate and so not rigorous numerical analysis of the problem was carried out by Colmenero *et al.* [13]. Moreover, the treatments of Matusita and Sakka [14] and Doulah [15, 16], which are not based on the Avrami–Erofe'ev model, are unable to determine all the kinetic parameters in question.

In order to get over this impasse, the argument of this paper concerns the development of a new method of analysis of DTA data, which does not present the above restrictions, because of its rigorous derivation. Other important features of the present method are the great simplicity and the requirement of a small number of experimental determinations.

2. Theory

In a previous paper, Borchardt and Daniels [17] derived a theory concerning the application of the DTA technique to the study of the kinetics of reactions in solution. Their work was based on a series of assumptions perfectly fulfilled by the reactions occurring in the liquid state, but, by choosing the appropriate experimental conditions, we may also use it in the solid phase reactions. The more problematic assumptions for the application of the theory stated by Borchardt and Daniels to solids were:

(a) the temperature in the DTA cells must be uniform. This is not generally true when the cells are filled with solid materials, but the inhomogeneities in temperature can, in practice, be neglected if the volume of the samples is very small. So, the use of microcells permits the fulfilment of this assumption for solid-state reactions;

(b) the heat capacities and the heat-transfer coefficient of the sample and of the reference must be equal, i.e. C_{p} (sample) $= C_{\text{p}}$ (reference) and K (sample) $= K$ (reference). In this case, an extended dilution of the sample with the inert reference material and the application of the same filling procedure for the two cells leads to very small and negligible differences in the heat capacities and in the heat-transfer coefficients of the reference and sample.

So, when these two experimental conditions are satisfied, the general Borchardt and Daniels' theory is applicable to the reactions in the solid state. In particular, the following equation is still valid:

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{N_0}{K\mathrm{A}}\left(C_{\text{p}}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T\right), \qquad (4)$$

where N is the number of the reacting moles, N_0 the initial number of moles, C_{p} the heat capacity of both sample and reference, K the heat-transfer coefficient of the two specimens, ΔT the temperature difference between them and $\mathrm{A} = \int_0^\infty \Delta T \mathrm{d}t$ is the area under the DTA peak.

On the basis of the previous assumptions we obtain:

$$-\frac{1}{N_0}\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}t},$$

so

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{K\mathrm{A}}\left(C_{\text{p}}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T\right). \qquad (5)$$

If, in the DTA analysis, the heating rate, h, is constant, we have

$$T = ht + T_0,$$

when T_0 is the starting (room) temperature.

Hence, $\mathrm{d}t = \mathrm{d}T/h$ and by substituting Equation 5 we obtain:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{K\mathrm{A}}\left(\frac{\mathrm{d}\Delta T}{\mathrm{d}T}C_{\mathrm{p}}\,h + K\Delta T\right). \tag{6}$$

If the DTA pattern is obtained on an $X-Y$ recorder, we have $\Delta T = \Delta T(T)$. At the maximum of a positive or negative peak, according to exothermic or endothermic reactions, the following condition is fulfilled because of the obvious continuousness of the $\Delta T = \Delta T(T)$ function:

$$\left(\frac{\mathrm{d}\Delta T}{\mathrm{d}T}\right)_{\max} = 0.$$

Equation 6 is then reduced to:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max} = \frac{1}{\mathrm{A}}(\Delta T)_{\max}$$

or

$$(\Delta T)_{\max} = \mathrm{A}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\max}. \tag{7}$$

It is crucial to underline that this relationship of direct proportionality is strictly valid only at the peak maximum. Equation 7 then does not express that at the peak maximum the reaction rate is maximum, and so the present treatment is not submitted to Reed's critics.

Now we suppose that the reaction we are examining is described by the Avrami–Erofe'ev Equation 2. We can express:

$$\alpha = 1 - \exp\left[-(kt)^n\right]. \tag{8}$$

If the reaction in question follows an Arrhenius-type trend, during the DTA run with constant heating rate, the rate coefficient, k, depends on time. In fact it may be written:

$$k = A\exp\left[\pm\frac{E_{\mathrm{act}}}{R(ht+T_0)}\right].$$

From Equation 8, it is now possible to differentiate with respect to:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \exp\left[-(kt)^n\right]\left[nk^n\frac{E_{\mathrm{act}}ht^n}{R(ht+T_0)^2} + nk^nt^{n-1}\right]$$

$$= \exp\left[-\frac{k(T-T_0)}{h}\right]^n\left[nk^n(T-T_0)^n\left(\frac{1}{h}\right)^n \times\frac{E_{\mathrm{act}}h}{RT^2} + nk^n\cdot\left(\frac{1}{h}\right)^{n-1}(T-T_0)^{n-1}\right].$$

We can set $S = T - T_0$, $\beta = E_{\mathrm{act}}/R$ and then:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \exp\left(-\frac{kS}{h}\right)^n\left[nk^nS^n\left(\frac{1}{h}\right)^{n-1}\frac{\beta}{T^2} + nk^n\left(\frac{1}{h}\right)^{n-1}S^{n-1}\right].$$

At the peak maximum, Equation 7 is valid and so:

$$(\Delta T)_{\max} = \mathrm{A}\exp\left[-\frac{kS_{\mathrm{m}}}{h}\right]^n\left[nk^nS_{\mathrm{m}}^n\left(\frac{1}{h}\right)^{n-1}\frac{\beta}{T^2} + nk^n\left(\frac{1}{h}\right)^{n-1}S_{\mathrm{m}}^{n-1}\right], \tag{9}$$

where $T_{\mathrm{m}} = T$ at the maximum, and $S_{\mathrm{m}} = S$ at the maximum.

It is now possible to differentiate ΔT with respect to T and evaluate $\mathrm{d}\Delta T/\mathrm{d}T$. The maximum condition supplies in this way an equation, in which the unknown quantity k can be obtained. Hence:

$$k = \frac{h}{S_{\mathrm{m}}}\left[\frac{(n\beta^2/T_{\mathrm{m}}^4)\,S_{\mathrm{m}}^2 - (2\beta/T_{\mathrm{m}}^3)\,S_{\mathrm{m}}^2 + (2n\beta/T_{\mathrm{m}}^2)\,S_{\mathrm{m}} + n - 1}{(n\beta^2/T_{\mathrm{m}}^4)\,S_{\mathrm{m}}^2 + (2n\beta/T_{\mathrm{m}}^2)\,S_{\mathrm{m}} + n}\right]^{1/n}. \tag{10}$$

By considering the magnitude orders of the various terms (T_{m} and $S_{\mathrm{m}} \sim 10^2$, $\beta \sim 10^4$) it is obvious that n and 1 are surely negligible. Equation 10 is easily transformed in

$$k = \frac{h}{S_{\mathrm{m}}}\left[1 - \frac{2S_{\mathrm{m}}T_{\mathrm{m}}}{n\beta S_{\mathrm{m}} + 2nT_{\mathrm{m}}^2}\right]^{1/n}. \tag{11}$$

On the basis of Equation 2 we reach the final relationship

$$h = AS_{\mathrm{m}}\exp\left(-\frac{\beta}{T_{\mathrm{m}}}\right)\left[1 - \frac{2S_{\mathrm{m}}T_{\mathrm{m}}}{n\beta S_{\mathrm{m}} + 2nT_{\mathrm{m}}^2}\right]^{-1/n}. \tag{12}$$

This complex equation connects the kinetic parameters n, β, A with the experimental quantities h, T_{m}, S_{m}. It is now possible to record several DTA patterns at different constant heating rates and the analysis of the peak leads to the knowledge of T_{m} and S_{m} for each pattern. Now, by means of a non-linear regression algorithm, the fitting of Equation 12 allows the simultaneous determination of all the kinetic parameters.

3. Results

In order to check the correctness of the method described above, we have compared isothermal data for a reaction which is known to follow the Avrami–Erofe'ev equation, i.e. the crystallization of the $Li_2O \cdot 2SiO_2$ glass, with the kinetic parameters calculated with the best fit of Equation 12. On these grounds, 15 g reagent grade Li_2CO_3 and SiO_2 in a 1:2 molecular ratio were melted at 1500° C for 2 h in an electrically heated muffle furnace under air atmosphere. The melt was quenched on a stainless steel plate and gave rise to a very transparent glass. The sample was then very carefully ground in an agate mortar. The resulting DTA powder patterns were then recorded, using a Linseis L62 thermoanalyser equipped with very small crucibles and with crystalline Al_2O_3 as reference. The glassy sample was each time diluted with Al_2O_3 and the two crucibles were filled in the same way. Five analyses were carried out and the different heating rates are reported in Table I. Each pattern exhibited an intense exothermic peak, always preceded by the characteristic "annealing dip" representing the glass transition. The temperatures of the peak's maxima are also summarized in Table I.

The fitting of Equation 12 was carried out by means of a computer program (BARD algorithm) based on the Gauss–Newton non-linear regression method [18]. The program needs a set of initial guesses for the parameters. In order to obtain a simple derivation of the initial set of approximate parameters, it is worth noting that Equation 12 can be written as

$$A^n = \frac{h^n}{S_m^n} \exp\left(\frac{n\beta}{T_m}\right)\left[1 - \frac{2S_m T_m}{n\beta S_m + 2nT_m^2}\right]. \tag{13}$$

The values of S_m, T_m, n and β make the term $2S_m T_m/(n\beta S_m + 2nT_m^2)$ always negligible with respect to 1. In this way, Equation 13 becomes:

$$A = \frac{h}{S_m} \exp\left(\frac{\beta}{T_m}\right).$$

TABLE I Experimental parameters of the DTA patterns

h (K min^{-1})	T_m (K)	S_m (K)
1	790.65	498.5
2	810.65	518.5
5	826.15	533.0
10	843.65	550.5
20	861.15	568.0

By taking logarithms we have

$$\ln\left(\frac{S_m}{h}\right) = \frac{\beta}{T_m} - \ln A.$$

Now, if we plot $\ln(S_m/h)$ against $1/T_m$, the slope and the intercept of the least squares calculated straight line allow a good approximate evaluation of β and A, which can supply an initial set of guesses. Because of the narrow range of variability of n which has a physical meaning only when included between 0 and 4, it is possible to choose in any case $n = 2$ as a good initial guess.

In our case, the guesses were fixed at $A = 1 \times 10^{11}$ sec^{-1}, $\beta = 30\,000$ K and $n = 2$; in fact this choice is not critical, because different guesses can only modify the number of iterations required for the achievement of the best fit solution, but not the quality of the fitting itself.

The results of the calculations are: $A = 6.64 \times 10^{11}$ sec^{-1}; $\beta = 27880$ K, i.e. $E_{act} = 231.68$ kJ mol^{-1}; $n = 1.77$.

The most commonly accepted values of the kinetic parameters for the crystallization of the $Li_2O \cdot 2SiO_2$ glass are those reported by Freiman and Hence [19] which concern the overall process of crystallization of $Li_2Si_2O_5$ and which can be summarized as: $E_{act} = 234$ kJ mol^{-1}; $n = 1.7$. It is known that this value of n represents a crystallization with a rod-growth occurring with a constant nucleation rate. Unfortunately, no value is available for the Arrhenius pre-exponential factor of the overall process. A comparison of the two sets of results shows the total reliability of the proposed method of evaluation, which in addition proves much simpler than the isothermal ones. Moreover, the present check confirms the crystallization mechanism proposed by Freiman and Hench.

4. Conclusions

The validity has been shown, on the basis of rigorous theoretical considerations, of a quantitative relationship concerning all the kinetic parameters which are necessary for the complete characterization of a reaction following the Avrami–Erofe'ev equation. Furthermore, an experimental check of our method, based on the comparison between the isothermal data and the present DTA data for the crystallization of the $Li_2O \cdot 2SiO_2$ glass has proved completely successful. The complete and accurate knowledge of the fundamental quantities ruling a solid-state reaction leads either to basic considerations concerning the reaction mechanism, or to a detailed prevision of the reaction trend, with important technological repercussions, i.e. in the field of glass ceramics.

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References

1. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
2. *Idem, ibid.* **8** (1940) 212.
3. *Idem, ibid.* **9** (1941) 177.
4. B. V. EROFE'EV, *Compt. Rend. Dokl. Acad. Sci. USSR* **52** (1946) 511.
5. H. E. KISSINGER, *Analyt. Chem.* **29** (1957) 1702.
6. *Idem, J. Res. Nat. Bur. Stand.* **57** (1956) 217.
7. R. L. REED, L. WEBER and B. S. GOTTFRIED, *Ind. Eng. Chem. Fundls* **4** (1965) 38.
8. F. O. PILOYAN, I. U. RYABCHIKOV and O. S. NOVIKOVA, *Nature (London)* **212** (1966) 1229.
9. J. ŠESTÁK, *Phys. Chem. Glasses* **15** (1974) 137.
10. A. MAROTTA and A. BURI, *Thermochim. Acta* **25** (1978) 155.
11. A. MAROTTA, A. BURI and F. BRANDA, *J. Mater. Sci.* **16** (1981) 341.
12. J. M. CRIADO and A. ORTEGA, *Thermochim. Acta* **46** (1981) 213.
13. J. COLMENERO, J. ILARRAZ and J. M. BARANDIARÁN, *ibid.* **35** (1980) 381.
14. K. MATUSITA and S. SAKKA, *ibid.* **33** (1979) 351.
15. M. S. DOULAH, *ibid.* **42** (1980) 373.
16. *Idem, ibid.* **35** (1980) 263.
17. H. J. BORCHARDT and F. DANIELS, *J. Amer. Chem. Soc.* **79** (1957) 41.
18. J. L. KUESTER and J. H. MIZE, "Optimization Techniques with Fortran" (McGraw-Hill, New York, 1973) p. 218.
19. S. W. FREIMAN and L. L. HENCH, *J. Amer. Ceram. Soc.* **51** (1968) 382.

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