Journal of Thermal Analysis, Vol. 54 (1998) 399-406

DETERMINATION OF THE KINETIC PARAMETERS OF CHEMICAL REACTIONS ON THE BASIS OF NON-ISOTHERMAL MEASUREMENTS
A critical review

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Abstract

A detailed analysis is presented of the applicability of several dependences commonly used for the determination of activation energies from non-isothermal measurements. Reactions proceeding according to different kinetic equations are simulated and the validity of the activation energy values obtained is discussed. The general conclusion is drawn that none of the examined dependences should be used to determine the activation energy. For a rough estimation of activation energy, the Kissinger equation can be applied according to Ockham's razor.

Keywords: activation energy, kinetics, non-isothermal measurements

Introduction

The kinetic parameters of reactions are frequently determined on the basis of non-isothermal measurements of the reaction kinetics, especially when processes not involving a change in mass are concerned. Usually, a complete kinetic analysis of the process is not performed, and only the activation energy of the reaction is calculated as the parameter essential from the point of view of the investigated mechanism of the reaction. One possible way to determine the energy of activation is to make use of the temperature peak changes that occur during DTA measurements at different heating rates. Application of this method is possible if the reaction (conversion) is a single-stage process.

Several dependences which link together the temperature of the DTA peak (T_m) and the heating rate (β) with the activation energy (E_a) of the reaction are given in Table 1. The Kissinger equation (code A) has been derived for chemical reactions [1] running according to an n-th order kinetic equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

1418–2874/98/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

where α is the degree of conversion, t is time and k is the reaction rate constant, but the expression obtained does not depend on the order of the reaction.

Table 1 Equations applied for determination of activation energy from DTA peak

Equation code	Equation	Characteristics
A	$\ln(\beta/T_m^2) = -E_a/RT_m + \text{const.}$	Kissinger equation, independent of kinetics of process
B	$\ln(DTA) = \text{const.} - E_a/RT$	Piloian equation, independent of kinetics of process
C	$1.5\ln(\beta) = -E_a/RT_m + \text{const.}$	for process described by $\alpha = 1-\exp(-kt^{1.5})$
D	$\ln(\beta^2/T_m^2) = -E_a/RT_m + \text{const.}$	for process of bulk nucleation and one-dimensional growth of nuclei
E	$\ln(\beta^3/T_m^2) = -2E_a/RT_m + \text{const.}$	for process of bulk nucleation and two-dimensional growth of nuclei
F	$\ln(\beta^4/T_m^2) = -3E_a/RT_m + \text{const.}$	for process of bulk nucleation and three-dimensional growth of nuclei

Dependence A is widely used to evaluate the activation energy for any chemical reaction. The Piloyan equation [2] (code B) does not take into account a specific reaction mechanism, but was constructed with the single assumption that the DTA signal in the DTA curve is at every moment proportional to the reaction rate. Dependence C was derived for a reaction which proceeds according to the Mehl-Johnson-Avrami kinetic equation [3]. Dependences D, E and F were obtained on the basis of the kinetic equation describing the crystallization of glass:

$$\frac{d\alpha}{dt} = A\beta^{-(q-1)}(1-\alpha)^p \exp\left(-\frac{mE_a}{RT}\right)$$

where m, p and q are parameters connected with the mechanism of crystallization, R is the gas constant, T is temperature, and A is a constant.

In fact, the above equation applied to data obtained under non-isothermal conditions corresponds to the Mehl-Johnson-Avrami (MJA) equation for kinetic data obtained under isothermal conditions. Dependences A and C–F were derived on the assumption that the reaction reaches the maximum rate at the temperature of the DTA peak.

Overall, therefore, dependences A and B allow calculation of the activation energy of any process, even if its mechanism or the kinetic equation describing the process is unknown, while dependences C–F take into account the mechanism of the process.

In paper [6], devitrification of glasses of composition $2CaO–Al_2O_3–SiO_2$ was examined and the devitrification activation energy was determined on the basis of dependences A and C. The activation energy values obtained from dependences A and C were 731 and 1128 kJ mol^{-1}, respectively. It was impossible to establish which of these two values is correct as a significant linear correlation was observed for both equations and the statistical test did not indicate which of the obtained values is the more probable. Additionally, the activation energy values obtained from dependences A and C were not the same as the values calculated directly from the MJA equation, which was found to describe the examined process. It is worth noting that in paper [3], for the glasses of composition given above, significantly different activation energy values were found: 436 kJ mol^{-1} using dependence A (value calculated by the authors of the present paper on the basis of data given in [3]), and 690 kJ mol^{-1} using dependence C.

In consequence of the considerable differences between the activation energy values estimated from dependences A and C, the goal of the present work is to test the applicability of all the equations listed in Table 1, which are frequently used to determine activation energies from DTA peaks, and to establish the accuracy of determination of activation energy and the real physical meaning of estimated values usually treated as activation energies. To make such a test as objective as possible, a model of a chemical reaction with a known heat effect, kinetic equation and activation energy has been assumed, and the DTA curves for this reaction have been simulated.

Modeling DTA curves

DTA curves were computed for the reaction proceeding according to several different kinetic equations:

1) The MJA kinetic equation:

$$\alpha = 1 - e^{-kt^n} \tag{1}$$

where parameter n equals 1.0, 1.1, 1.2, 1.3, 1.4 and 1.5, depending on the mechanism of the reaction.

2) The Ginstling-Brounstein (GB) equation:

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt \tag{2}$$

3) The volume contraction (VC) equation:

$$1 - (1 - \alpha)^{1/3} = kt \tag{3}$$

The DTA signal represents the difference between the sample temperature T_S and reference temperature T_R at every moment of the reaction:

$$\mathrm{DTA}(t) = T_S(t) - T_R(t) \tag{4}$$

In the simplest case, to simulate the DTA peak profile of a reaction, dependences describing the rates of sample temperature changes and reference temperature changes have to be found:

$$\frac{dT_S(t)}{dt} = k_S\left[T_F(t) - T_S(t)\right] + K_S\frac{d\alpha}{dt} \tag{5}$$

$$\frac{dT_R(t)}{dt} = k_R\left[T_F(t) - T_R(t)\right] \tag{6}$$

where T_F is the furnace temperature, K_S is a coefficient proportional to the heat of conversion, k_S is a coefficient of the furnace – sample heat conduction, and k_R is a coefficient of the furnace, the reference heat conduction.

It is obvious that when the reaction proceeds under conditions of linear increase of heating rate, the temperature of the furnace at moment t is

$$T_F(t) = T_o + \beta t \tag{7}$$

where T_o is the temperature at t=0. Insertion of expression (7) into Eq. (6) and solving the differential equation leads to the following dependence for $T_R(t)$

$$T_R(t) = T_o + \beta t + \frac{\beta}{k_R}(e^{-k_R t} - 1) \tag{8}$$

According to Eq. (5), the change in T_s in time depends on the kinetic equation, which corresponds to the chemical reaction. For instance, for the MJA kinetic equation, Eq. (5) has the following form:

$$\frac{dT_S(t)}{dt} = k_S\left(T_o + \beta t - T_S(t)\right) + K_S\left[n\left(\frac{k_o}{n}\right)^n e^{-\frac{nE_a}{RT_S(t)}} t^{(n-1)} \exp\left[-\left(\frac{k_o}{n}\right)^n e^{\frac{nE_a}{RT_S(t)}} t^n\right]\right] \tag{9}$$

under the assumption that the temperature dependence of the rate constant is given by the Arrhenius equation: $k=k_o e^{-(E_a/RT)}$.

The analytical solution of differential equation (9) does not exist, and therefore the numerical methods of solving this equation should be applied. On the basis of the numerical solution in the whole time interval of the reaction $T_s(t)$ can be calculated for given kinetic parameters and defined conditions of kinetic measurements. An analogous procedure can be applied for the GB and VC kinetic equations.

On the basis of the determined dependences $T_S(t)$ and $T_R(t)$, DTA scans have been simulated. In all simulations, the same values of heat conduction coefficients k_S and k_R and the same value of K_S were applied. The value of k_o was chosen so that the height and width of the DTA peaks were close to those obtained in measurements in work [5].

DTA curves were simulated for reactions proceeding according to the MJA equation with parameters n=1.0, 1.1, 1.2, 1.3, 1.4 and 1.5, and also for reactions running according to the GB and VC equations. For every equation, different activation energy values from the range 100–600 kJ mol^{-1} were taken for simulations. The obtained DTA curves were then used to determine the activation energy on the basis of equations A–F from Table 1.

Results and discussion

Figure 1 shows, by way of example, the computed DTA peak profiles for a heating rate of 8 K min^{-1} for reactions proceeding according to Eqs (1), (2)

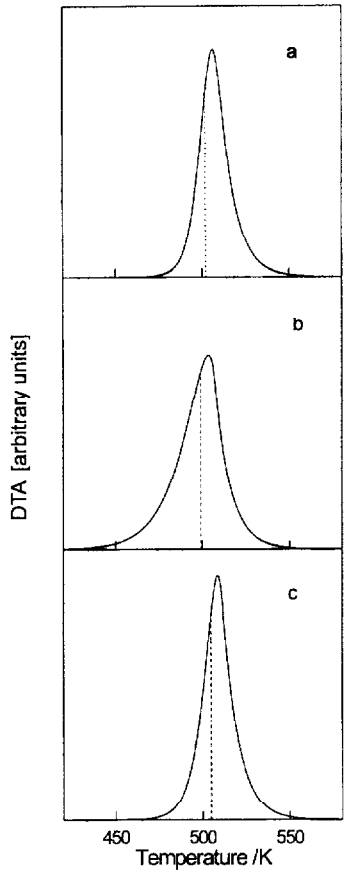

Fig. 1 Computed DTA scans of reactions proceeding according to different kinetic equations: a) Mehl-Johnson-Avrami equation, n=1.2, b) Ginstling-Brounstein equation, c) volume contraction equation. Initial value of activation energy used in calculations: 300 kJ mol^{-1}. All DTA scans were calculated for a heating rate of 8 K min^{-1}. The dashed lines indicate the temperature calculated for the maximum reaction rate

and (3). The activation energy used in the calculations for these reactions was 300 kJ mol^{-1}. It can be seen that the temperature for the maximum reaction rate does not coincide with the temperatures of the DTA peaks. This can be considered evidence that the application of dependences A–F for the calculation of activation energy is doubtful. Nevertheless, for all simulated reactions, the energy of activation was evaluated. The left-hand sides of A and C–F as functions of T_m^{-1}, and the left-hand side of B as a function of T^{-1}, were found to be straight lines (Fig. 2) with regression coefficients higher than 0.999, so there was no criterion to distinguish between values of E_a evaluated from the slopes of these lines. The calculated values of E_a for all assumed mechanisms of reaction differ significantly from those initially used for simulations. Table 2 lists the results of estimation of E_a for an initial activation energy of 300 kJ mol^{-1}.

It may be presumed that the best estimates of E_a should be obtained from Eqs C, D, E and F, based on Eq. (1). However the results in Table 2 do not allow such a conclusion. The Piloyan equation (B) also produces far worse values of E_a than those initially used for estimation.

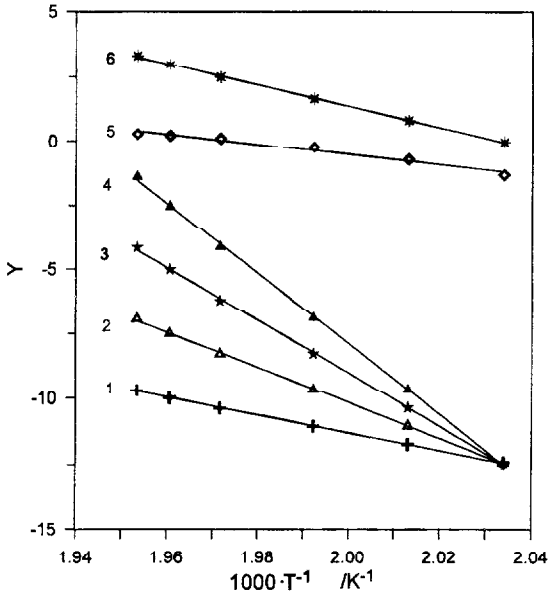

Fig. 2 Plots of dependences used for determination of activation energy from DTA peaks:
1) $\ln(\beta/T_m^2) = -E_a/(RT_m) + \text{const.}$, 2) $\ln(\beta^2/T_m^2) = -E_a/(RT_m) + \text{const.}$,
3) $\ln(\beta^3/T_m^2) = -2E_a/(RT_m) + \text{const.}$, 4) $\ln((\beta^4/T_m^2 = -3E_a/(RT_m) + \text{const.}$,
5) $\ln(\text{DTA}) = \text{const.} - E_a/(RT)$, 6) $1.5\ln(\beta) = -E_a/(RT_m) + \text{const.}$
Y: values of left-hand side of plotted equations. T_m: DTA peak temperature.
All plots were made for simulated DTA curves for a reaction running according to the Mehl-Johnson-Avrami equation with n=1.2

Table 2 Energies of activation calculated on the basis of the dependences listed in Table 1 for simulated reactions with different mechanisms (different kinetic equations), but the same initial value of energy of activation, 300 kJ mol^{-1}

Kinetic equations used for simulations	Calculated values of activation energy/kJ mol^{-1}					
	Eq. A	Eq. B	Eq. C	Eq. D	Eq. E	Eq. F
$\alpha = 1 - \exp(-kt)$	256	285–297	264	520	392	349
$\alpha = 1 - \exp(-kt^{1.1})$	265	319–337	301	538	406	362
$\alpha = 1 - \exp(-kt^{1.2})$	275	354–379	341	560	422	376
$\alpha = 1 - \exp(-kt^{1.3})$	288	391–427	385	584	440	392
$\alpha = 1 - \exp(-kt^{1.4})$	299	432–475	431	607	457	408
$\alpha = 1 - \exp(-kt^{1.5})$	309	478–555	477	628	473	421
$1 - (1 - \alpha)^{1/3} = kt$	276	286–297	–	–	–	–
$1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt$	250	133–137	–	–	–	–

Relatively good estimates of activation energy were obtained with the Kissinger equation (Table 3).

In fact, the shape and the temperature of a DTA peak depend on many factors. Some of them lead to overestimation and other to underrating of the obtained value assumed as activation energy in relation to the true value of the activation energy of the reaction. If only some of factors mentioned above are taken into ac-

Table 3 Energy of activation calculated by using Kissinger equation for simulated reactions with different mechanisms (different kinetic equations) and different initial values of energy of activation E_a

Initial E_a/ kJ mol^{-1}	Values of activation energy calculated from Kissinger equation/kJ mol^{-1} Kinetic equation used for simulation							
	$\alpha = 1 - \exp(-kt^n)$						*	**
	n=1.0	n=1.1	n=1.2	n=1.3	n=1.4	n=1.5		
100	86.5	88.6	90.4	92.8	95.4	97.3	90.2	85.5
200	171	176	182	187	193	201	182	168
300	256	265	276	288	300	310	277	250
400	346	360	375	390	407	426	376	335
500	438	457	477	502	521	550	478	422
600	529	555	583	613	641	686	591	509

* $1 - (1 - \alpha)^{1/3} = kt$

** $1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt$

count in the dependences used for the estimation of E_a, a systematic error can easily be generated as a consequence of an asymmetrical choice of factors causing an overestimation or an underrating of E_a. Thus, the Kissinger equation, which is the simplest one, gives the best results.

Additionally, it is worth noting that, in real DTA measurements, the mechanism of the reaction and the kinetic equation describing this mechanism are generally unknown. By using dependences A–F, it is possible to estimate a set of values of E_a with high accuracy, but there is no criterion to establish which, if any of them, is the true one.

In conclusion, non of equations A–F should be used for the determination of activation energy. For a rough estimation of activation energy, according to Ockham's razor, the Kissinger equation can be applied.

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This work was supported by the State Committee for Scientific Research in Poland.

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