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Application of non-linear heating regime for the determination of activation energy and kinetic parameters of solid-state reactions

K.V. Tomashevitch[a], S.V. Kalinin[a], A.A. Vertegel[a,*], N.N. Oleinikov[a], V.A. Ketsko[b], Yu.D. Tretyakov[a]

[a] *Inorganic Chemistry Division, Chemistry Department, Moscow State University, Moscow, Russia*
[b] *Institute of General and Inorganic Chemistry, Russian Academy of Science, 119899, V-234, Vorob'evy Hills, Moscow, Russia*

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Abstract

In the present research, we suggested non-linear heating regime for the thermogravimetric (TG) determination of kinetic parameters of solid-state reactions. The method is based on the application of a hyperbolic heating mode. The method allows the reaction activation energy and kinetic function to be obtained from a series of non-isothermal experiments. Kinetics of the model solid-state reaction $Fe_2O_3+Li_2CO_3=2LiFeO_2+CO_2$ was investigated by the suggested method. The kinetic parameters obtained are in a good agreement with the reference data. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of the kinetic parameters of solid-state reactions, such as the kinetic equation, activation energy, etc. gives valuable insight in the mechanism of the process. A number of experimental techniques can be applied for the evaluation of kinetic parameters. Among others one should mention quantitative X-ray diffraction analysis, elemental analysis, thermomagnetic analysis, etc. [1–3]. Nevertheless, the main and probably the most convenient way is thermal analysis, which allows one to observe the kinetics of the process continuously [4,5].

Traditionally, all the variety of thermoanalytical methods can be subdivided into two categories – isothermal and non-isothermal methods. The latter are usually performed at linear heating rates $T=T_0+\beta\tau$, where T is temperature, T_0 the initial temperature, τ time, and β the heating rate [4].

In order to obtain kinetic data from isothermal experiments a series of measurements should be performed. Taking into account the exponential dependence of the kinetic constant on temperature, this imposes certain limits on the range of kinetic parameters possible for direct observation. The other disadvantage is that partial mass loss occurs during the initial stage of the reaction when heating to experimental temperature and the analysis of the series of isotherms may yield incorrect results [1,6].

These difficulties may be avoided by use of non-isothermal methods [7,8]. However, the analysis of polythermal data is a very complicated task. A number of techniques have been proposed to extract this information from the experimental data. Most of the techniques suggested so far are based on the analysis

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*Corresponding author. Tel.: +7-95-939-5245; fax: +7-95-939-0998; e-mail: al@inorg.chem.msu.ru

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of several points on TG curves [9–14]. Therefore, the main advantage of the TGA method, namely the possibility to observe the reaction kinetics continuously, is lost. Moreover, the extraction of the kinetic equation from data obtained in linear heating modes becomes extremely difficult due to the fact that the rate constant exponentially depends on the reciprocal temperature [7,8]. In the present paper, we demonstrate that the application of the hyperbolic heating rates substantially facilitates mathematical analysis of experimental data.

2. Theoretical

In the present research we consider a simple decomposition reaction

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}.$$

We assume that the kinetic equation $\partial\alpha/\partial\tau=f(\alpha,T)$ can be written down as:

$$\frac{\partial\alpha}{\partial\tau} = k_0 \exp\left(-\frac{E_{\text{A}}}{RT}\right) f(\alpha) \tag{1}$$

where α is the degree of conversion, k_0 the pre-exponential factor, E_{A} the activation energy, and $f(\alpha)$ the temperature independent kinetic function.

The validity of such factorization for homogeneous reactions seems to be well established [15]. In case of inhomogeneous reactions the correctness of Eq. (1) is more questionable [16]. However, it is well known that the temperature dependence of the kinetic constants for inhomogeneous solid-state reactions is well described by the Arrhenius law with a well-defined activation energy in the wide temperature intervals. Thus, Eq. (1) can be considered as a useful approximation [17,18].

As a result of polythermal TGA with traditionally used linear heating rate $T=T_0+\beta\tau$ one obtains the time dependence of the degree of conversion, α. At the same time, integration of Eq. (1) on the assumption of a linear heating rate reads:

$$\begin{aligned}\frac{1}{k_0}\int_0^{\alpha}\frac{\partial\alpha}{f(\alpha)} &= -\frac{T_0}{\beta}\exp\left(-\frac{E_{\text{A}}}{RT_0}\right) + \left(\frac{T_0+\beta\tau}{\beta}\right)\exp\left(-\frac{E_{\text{A}}}{R(T_0+\beta\tau)}\right) \\ &\quad -\frac{E_{\text{A}}}{R\beta}\left[Ei\left(-\frac{E_{\text{A}}}{RT_0}\right) - Ei\left(-\frac{E_{\text{A}}}{R(T_0+\beta\tau)}\right)\right],\end{aligned} \tag{2}$$

where $Ei(x)$ stands for the exponential integral of x, α is the degree of conversion corresponding to time τ.

The complicated functional form of the overall kinetic Eq. (2) makes the direct analysis of experimental data almost impossible. This fact gave rise to a number of approximations that have been described elsewhere [9–14,19].

However, provided the *reciprocal* temperature growth is a linear function of time

$$\frac{1}{T(\tau)} = \frac{1}{T_0} + \gamma\tau, \tag{3}$$

γ being the reciprocal heating rate constant, Eq. (1) can be integrated to the analytical function:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{k_0 R}{\gamma E_{\text{A}}}\exp\left(-\frac{E_{\text{A}}}{RT_0}\right) \times \left\{1-\exp\left(-\frac{E_{\text{A}}\gamma\tau}{R}\right)\right\} \tag{4}$$

It should be noted that Eq. (4) is rather simple and provides a convenient way for the determination of k_0 and E_{A} from the experimental data.

Taking into account Eq. (4), the activation energy E_{A} can be found from several (i=1,. . .,n) experiments with different γ_i without making any a priori assumptions about the functional form of $f(\alpha)$:

$$\begin{aligned}&\frac{1}{\gamma_1}\{1-\exp(E_{\text{A}}\gamma_1\tau_1/R)\} \\ &= \frac{1}{\gamma_2}\{1-\exp(E_{\text{A}}\gamma_2\tau_2/R)\} = \cdots \\ &= \frac{1}{\gamma_n}\{1-\exp(E_{\text{A}}\gamma_n\tau_n/R)\}.\end{aligned} \tag{5}$$

Calculation in this case gives the value of the activation energy for each value of α and, thus, may be useful if E_{A} slightly changes with the temperature.

The subsequent differentiation of the right- and left-hand sides of Eq. (4) with respect to τ yields the following expression for the non-isothermal rate of reaction:

$$f(\alpha) = \frac{\partial\alpha}{\partial\tau}\frac{1}{\{k_0\exp(-E_{\text{A}}/RT_0)\exp(-E_{\text{A}}\gamma\tau/R)\}} \tag{6}$$

This equation can be used to extract the quasi-isothermal kinetic function $f(\alpha)$ directly from the experimental data without any *a priori* assumptions on its functional form. In order to do this one should vary the magnitude of E_A as a parameter for different values of γ_i until the numerical values of the right-hand side in Eq. (6) coincide across the whole range of the degrees of conversion.

3. Experimental

In order to illustrate the suggested technique, the solid-state reaction between lithium carbonate and α-Fe_2O_3 (molar ratio 1 : 1) has been studied.

$$Fe_2O_3 + Li_2CO_3 = 2LiFeO_2 + CO_2$$

The system to be investigated was prepared by mixing equimolar quantities of ferric oxide α-Fe_2O_3 and lithium carbonate (reagent grade). The experiments were performed in air on the programmable thermobalances ULVAC (Sinku-Riko) with IR heating elements. The heating regimes were calculated according to Eq. (3) with T_0=573 K, to T=1273 K. The total times of reaction were 40 min, 1 h, 1.5 h, 2 h, and 3 h. These times will be used in the following discussion for identification of the corresponding TG experiments. The heating regimes are presented in Fig. 1. The TG experiments with different hyperbolic heating rates γ_i were reproduced twice. The same reaction mixture was used for all TG experiments. However, it should be noted that thermal and chemical history of initial hematite strongly influences kinetics of lithium orthoferrite formation [20,21].

4. Results

The reasons for choice of the lithium orthoferrite formation for illustration of hyperbolic heating rate technique are as follows. First, the solid-state reaction between hematite and lithium carbonate (molar ratio 1 : 1) is accompanied by gas evolution that makes it easy to follow its kinetics by thermogravimetric method. Second, this reaction is well studied in literature for wide range of temperature and conditions [22–32]. Its kinetic parameters, such as activation energy, formal reaction order, reaction equation are well established.

The experimental TG curves for lithium ferrite formation carried out with different hyperbolic heating rates γ_i are shown in Fig. 2. In all cases, the reaction starting temperature is ≈400°C that is in agreement with the Refs. [22–32]. As one could have

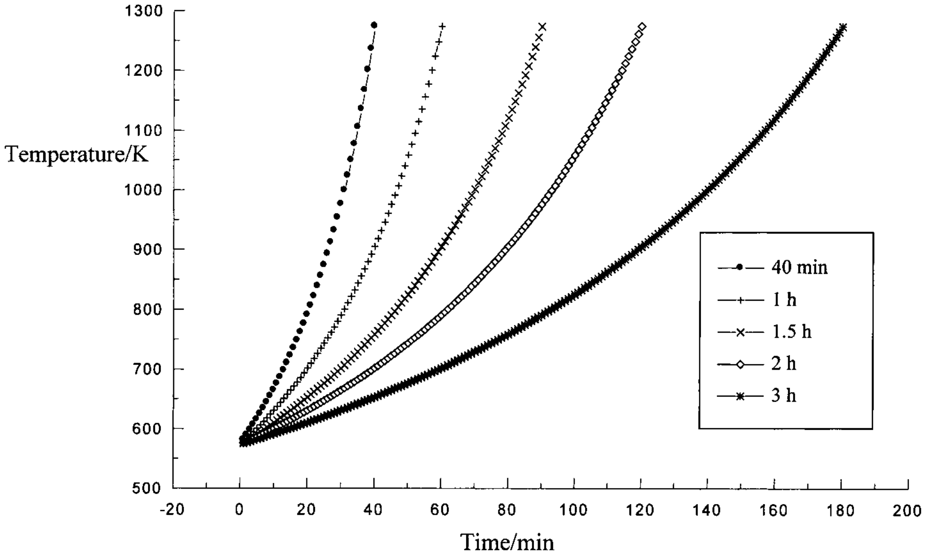

Fig. 1. Heating regimes calculated for different reciprocal heating rates γ_i.

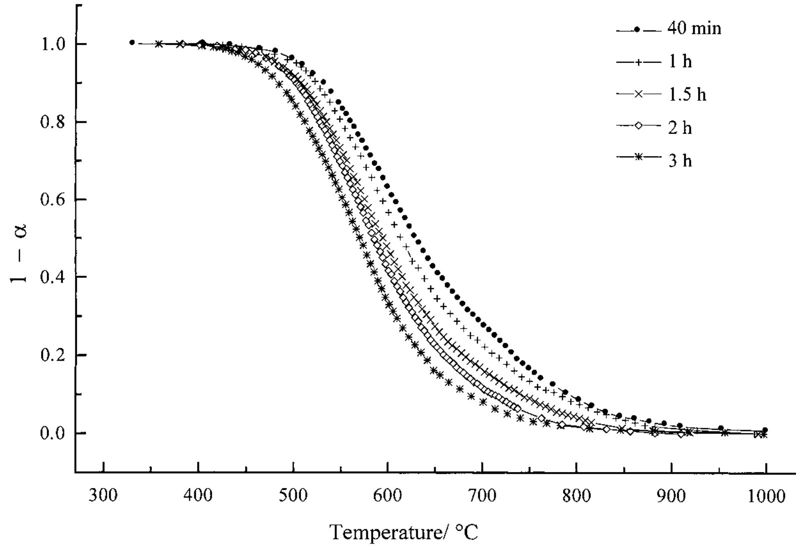

Fig. 2. Experimental TG curves for different reciprocal heating rates γ_i.

expected, the less the average heating rate, the higher is the degree of conversion corresponding to the certain temperature. The same trends are characteristic for polythermal experiments with the constant heating rate. At the same time, the reaction completes at ≈920°C for all studied magnitudes of γ_i.

5. Discussion

On the first step of analysis, the experimental TG curves were digitized and approximated by Eq. (4) following the assumption of Ref. [22] that $f(\alpha)=(1-\alpha)^n$. In this case the kinetic equation reads:

$$\frac{1}{1-n}\{(1-\alpha)^{1-n}-1\}=\frac{k_0 R}{\gamma E_A}\exp\left(-\frac{E_A}{RT_0}\right)\times\left\{1-\exp\left(-\frac{E_A\gamma\tau}{R}\right)\right\} \quad (7)$$

This approximation enabled to estimate the activation energy of the reaction and the formal order n for different heating rates γ_i. The values of the activation energy (see Table 1) lie within the range reported in the reference data (from 105 to 190 kJ/mol according to the Refs. [23,26,31,32]). The formal reaction orders reported in Ref. [22] vary from n=2.15 to n=2.71 depending on the synthetic route employed for the preparation of initial α-Fe_2O_3. The values of n obtained in the present paper are close to those reported in Ref. [22]. At the same time, in spite of the use of identical reaction mixtures, the formal reaction orders were found to change significantly depending on the value of γ_i. This probably points out that the assumption of the nth order reaction is not valid for the reaction under investigation, and may be used only formally. However, since the formal reaction order n>1, one can conclude that the process is diffusion-limited rather than reaction-limited.

Table 1
Kinetic parameters of lithium ferrite formation calculated from experimental data in assumption that the kinetic function obeys the nth order equation $f(\alpha)=(1-\alpha)^n$

Time, hour	Activation energy E_A/(kJ/mol)	Formal reaction order, n
40 min	175±2	3.01
1	183±3	2.83
1.5	171±1	2.63
2	177±2	2.48
3	148±2	2.40

The second approach to the analysis of experimental data is the direct application of Eq. (7) for the extraction of the kinetic function $f(\alpha)$. The TG curves were numerically differentiated, smoothed and plotted

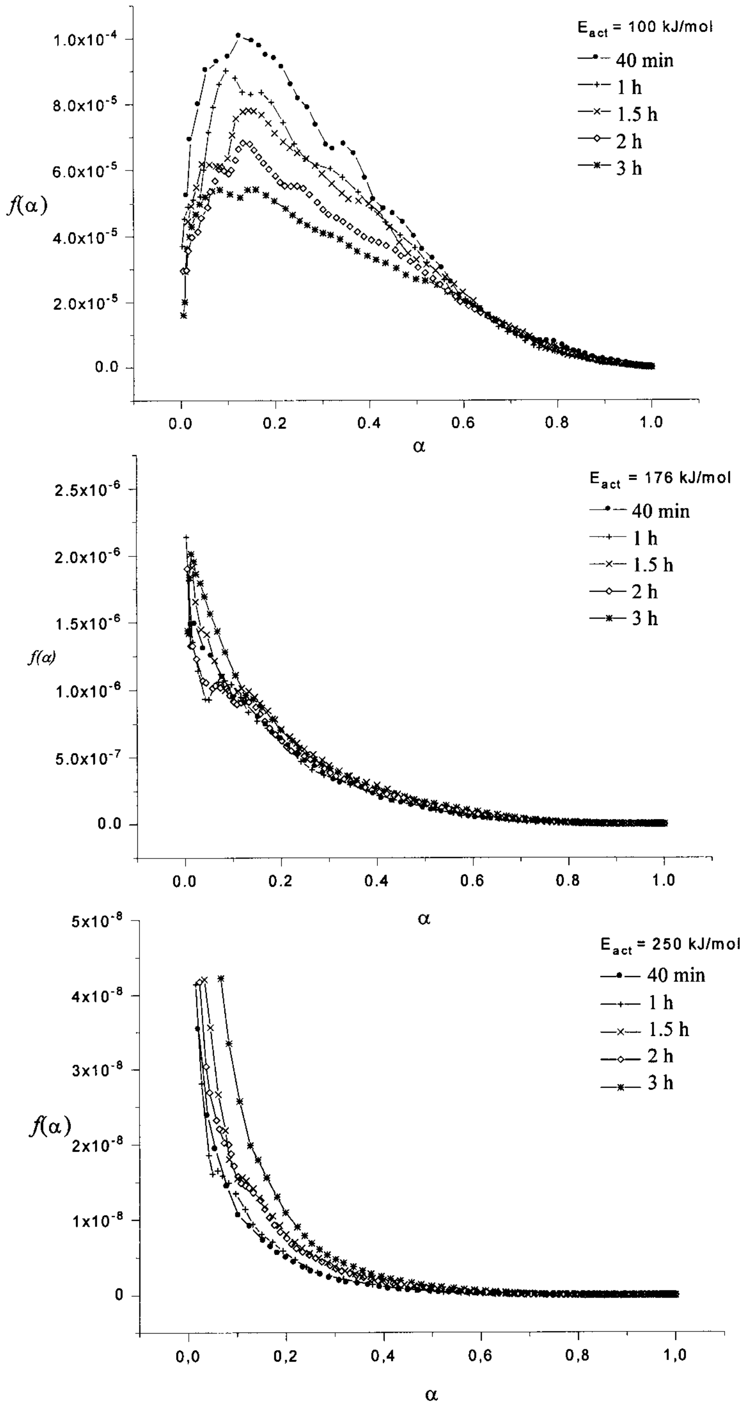

Fig. 3. (a,b,c) Kinetic functions $f(\alpha)$ for different values of parameter E_A.

in the coordinates corresponding to the right-hand side of Eq. (6) for different values of the activation energy. It is well seen that there exist an optimal value of E_A for which the mean square deviation between the experimental curves obtained for different γ_i reaches its minimal value. Our calculations show that this is achieved at E_A=176 kJ/mol (Fig. 3(b)), while for the other values the curves are significantly different (Fig. 3(a) and (c)). Thus, the curves shown in Fig. 3(b) correspond to the quasi-isothermal kinetic function $f(\alpha)$.

According to the majority of the reference data [23–25,27], kinetics of the reaction between α-Fe_2O_3 and Li_2CO_3 (1 : 1) in isothermal conditions follows Jander equation:

$$F(\alpha) = (1 - \sqrt[3]{1-\alpha})^2 = k_J\tau \tag{8}$$

for $T \geq 500°C$. However, for lower temperature ($425°C < T < 500°C$), experimental kinetic curves were successfully fitted by the contracting sphere model $F(\alpha) = (1 - \sqrt[3]{1-\alpha}) = k_{CS}\tau$, and thus the change of the reaction mechanism at $T \approx 500°C$ was supposed [28]. Studies of the reaction kinetics in polythermal regimes with linear heating rates also showed that quasi-isothermal kinetic function may be approximated by Jander equation [23]. Some authors used the Avrami equation: $F(\alpha)=\log[1/(1-\alpha)]=k\tau^m$; however they mentioned that this model may be applied only formally, since its assumptions are not valid for the reaction of lithium ferrite formation [26,29,30].

The quasi-isothermal kinetic function $f(\alpha)$ obtained from our experiments with hyperbolic heating rates was approximated by the following functions [1]:

Jander (J) model : $f(\alpha) = [dF(\alpha)/d\alpha]^{-1}$

$$= \frac{3(1-\alpha)^{2/3}}{2k_J(1-(1-\alpha)^{1/3})}$$

Ginstling–Brounstain (GB) model : $f(\alpha)$

$$= \frac{(1-\alpha)^{1/3}}{2k_{GB}(1-(1-\alpha)^{1/3})}$$

Dunwald–Vagner (DV) model : $f(\alpha)$

$$= \frac{6/\pi^2(1-\alpha)^2}{k_{DV}\ln(6/\pi^2(1-\alpha))}$$

Model of contracting sphere (CS) : $f(\alpha)$

$$= \frac{1}{k_{CS}}(1-\alpha)^{2/3}$$

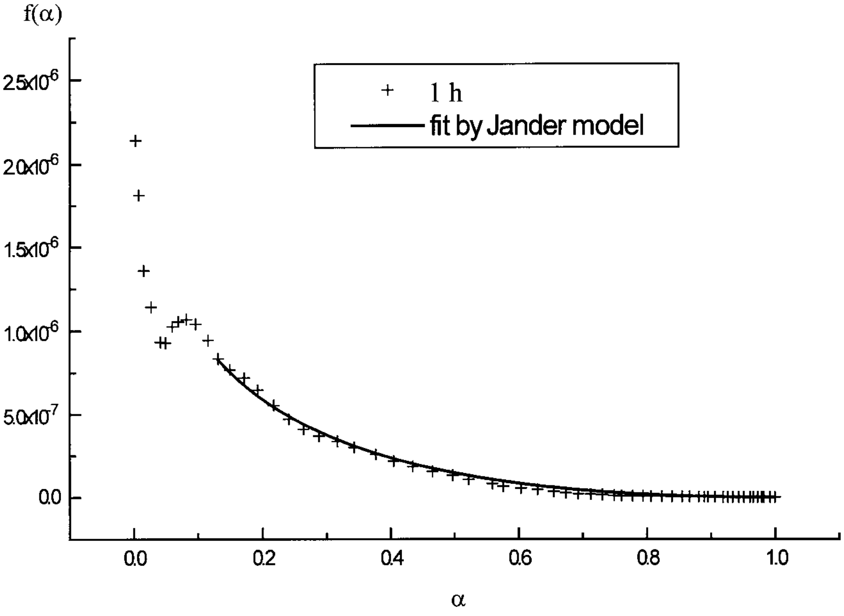

Fig. 4. Fit of kinetic function $f(\alpha)$ by the Jander equation: $f(\alpha)=3(1-\alpha)^{2/3}/2k_J(1-(1-\alpha)^{1/3})$.

The results of approximation show that for $\alpha \geq 0.15$ the best fit is observed for the use of the Jander equation (see Fig. 4). This corresponds well to the data obtained from isothermal and polythermal experiments in Refs. [23–25,27]. Experimental $f(\alpha)$ for $\alpha \geq 0.15$ may also be satisfactory approximated by GB model, while DV and CS models are not appropriate.

6. Conclusion

In the present research, we suggest the hyperbolic heating regimes for the determination of kinetic parameters of solid-state reaction from TG experiments. Analogously to the standard polythermal TGA, the advantage of this approach over isothermal kinetic studies is that it enables one to take into account the partial mass loss occuring at the initial stage of the reaction while heating up to experimental temperature. At the same time, the calculation of kinetic parameters from the experiments with hyperbolic heating rate is much easier than in case of linear heating rates. This approach was successfully applied for the analysis of the model solid-state reaction of lithium ferrite formation. The obtained value of the activation energy $E_{\mathrm{act}}=176\pm4$ kJ/mol is in a good agreement with the reference data. The kinetic function $f(\alpha)$ extracted from the experimental data well corresponds to the Jander model that is also well established for this reaction.

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