On the Li and Tang's isoconversional method for kinetic analysis of solid-state reactions from thermoanalytical data

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A criterion for the reaction mechanism as expressed by differential conversion function based on the Li and Tang's isoconversional method is suggested. The suitability of the use of Li and Tang's method for the estimation of a conversion dependent activation energy is discussed. © *2001 Kluwer Academic Publishers*

1. Introduction

Thermal analysis methods are widely used to investigate the thermal and/or thermooxidative degradation of materials. These methods allow us to put in evidence the processes occurring at the progressive heating of a given material. In many cases the nonisothermal kinetic parameters which can be used for the prediction of thermal endurance are estimated.

Recently [1–3] Li and Tang suggested a new isoconversional method for the analysis of non-isothermal thermoanalytical data. Li and Tang start from the classical rate equation:

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = A f(\alpha) \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where α is the conversion degree, t—the time, T—the reactant's temperature, β—the linear heating rate, A—the pre-exponential factor, E—the activation energy, R—the gas constant and $f(\alpha)$—the differential conversion function.

Integrating both side of the logarithmic form of Equation 1 with respect to α, we get:

$$\int_0^\alpha \left(\ln \frac{d\alpha}{dt}\right) d\alpha \equiv \int_0^\alpha \left(\ln \beta \frac{d\alpha}{dT}\right) d\alpha = -\frac{E}{R} \int_0^\alpha$$
$$\times \left(\frac{1}{T}\right) d\alpha + G(\alpha) \qquad (2)$$

where:

$$G(\alpha) \equiv \alpha \ln A + \int_0^\alpha [\ln f(\alpha)] \, d\alpha \qquad (3)$$

The plot of $\int_0^\alpha (\ln \frac{d\alpha}{dt}) \, d\alpha$ vs. $\int_0^\alpha (\frac{1}{T}) \, d\alpha$ for a given α and a set of β values, should be linear. From the slope of the straight line, the value of the activation energy can be obtained.

Unlike other integral isoconversional methods, such as Flynn-Wall-Ozawa (FWO) [4, 5] and Kissinger-Akahira-Sunose (KAS) [6, 7] methods, Li and Tang method (LT) [1–3] avoids the integration of the rate equation and correspondingly the use of various approximations for the temperature integral. According to Li and Tang, their method leads to errors lower than those corresponding to Friedman's method (FR) [8] according to which the activation energy is determined from the slope of the straight line $\ln \frac{d\alpha}{dt}$ vs. $(1/T)$, recorded for $\alpha = $ constant. Finally, Li and Tang's method does not require the knowledge of $f(\alpha)$ in order to evaluate E and can equally show the dependence of E on α.

In this paper we are going to analyze the possibility to use Li and Tang's procedure to find $f(\alpha)$ and A as well as its suitability for the cases of dependence of E on α.

2. A criterion to determine the analytical form of the differential conversion function

In a previous paper [9], some methods suggested by various authors used to find $f(\alpha)$ were analyzed. Besides, in that work a procedure to find the analytical form of $f(\alpha)$ was suggested. According to this procedure, the correct value of the activation energy is obtained using an isoconversional method. The correct analytical form of $f(\alpha)$ is that for which through an integral or differential procedure applied to each TG curve the same value of the activation energy is obtained. The main advantage of this procedure consists in the fact that improper analytical form of $f(\alpha)$ lead to significant differences between the values of the activation energy. Obviously, this criterion is suitable if E does not depend on α. In order to apply this criterion, Li and Tang's method should be associated with a differential or an integral procedure in such a way that a single TG curve could

give a pair of (E, A) values for each considered differential conversion function.

In the following, a criterion for finding $f(\alpha)$ using only Li and Tang's method is going to be suggested.

By plotting the straight lines $\int_0^\alpha (\ln \frac{d\alpha}{dt})\, d\alpha$ vs. $\int_0^\alpha (\frac{1}{T})\, d\alpha$ for a set of α values, the corresponding $G(\alpha)$ values could be found. Various forms of $f(\alpha)$ will be considered. For each of these forms, using relation (3) the dependence $\ln A$ vs. α is obtained. Obviously, the correct form of $f(\alpha)$ is that for which $\ln A$ does not practically depend on α. It turns out that through the application of this procedure, the triplet $(E, A, f(\alpha))$ could be found.

3. On the use of Li and Tang's method for cases in which E depends on α

At the derivation of relation (2), as well as of all relations which form the basis for the methods FWO and KAS, the activation parameters (E and A) are considered as independent of α. The only method of E estimation that does not use this hypothesis is that suggested by Friedman which uses directly the rate equation (Equation 1). This is the reason for our consideration that the methods FWO, KAS and LT are not suitable for the estimation of an activation energy that changes with the conversion degree. In previous works [9, 10] we have shown that if E depends on α, the integral methods lead to values of the activation energy which differ from those estimated using Friedman' method. The results reported by Li and Tang [1–3] for $CaCO_3$ and $SrCO_3$ confirm this statement. In these cases E depends on α and for each value of α, $E_{FR} \neq E_{FWO} \neq E_{KAS} \neq E_{LT}$. On the other hand, it was shown [9, 10] that if E does not depend on α, all the mentioned isoconversional methods give close values of E. This result was obtained by Li and Tang too [3] for the decomposition of CuO to Cu_2O and O_2.

The use of Li and Tang's procedure raises the problem of the lower integration limit. It is well known that in many cases, for each TG curve, the determination of the T value corresponding to $\alpha = 0$ is susceptible to rather high errors. The derivation of equation (2) does not impose as lower limit of integration $\alpha = 0$. This is the reason for we can consider that the integration of the logarithmic form of the rate equation with respect to α could be performed between α_1 and α:

$$\int_{\alpha_1}^{\alpha} \left(\ln \frac{d\alpha}{dt} \right) d\alpha = -\frac{E}{R} \int_{\alpha_1}^{\alpha} \left(\frac{1}{T} \right) d\alpha + G(\alpha) \quad (4)$$

where:

$$G(\alpha) = (\alpha - \alpha_1) \ln A + \int_{\alpha_1}^{\alpha} [\ln f(\alpha)]\, d\alpha \quad (5)$$

Obviously, if E does not depend on α, the values of E obtained for various values of α_1 should be equal. Besides, in such cases relations (4) and (5) can be used to determine the triplet $(E, A, f(\alpha))$ by applying the above suggested procedure.

The derivation of equation (4) is based on the supposition that E and A do not depend on α. But if the activation parameters depend on α, the value of E determined using Li and Tang's procedure is intermediate between $E(\alpha_1)$ and $E(\alpha)$. Thus it appears that for a given α, the E value depends on the lower limit of integration (α_1). Under such conditions one can expect that if E increases with α, E_{LT} for a given α, increases with (α_1). Consequently, the position of the curve E_{LT} vs. α in the space (E, α) could be switched by changing the value of (α_1). This dependence of E_{LT} on the lower limit of integration when E depends on α, determines the irrelevancy of comparison between E_{LT} values and the values of the activation energy determined from non-isothermal data by help of other isoconversional methods (FR, FWO, KAS). In these cases, the comparison between E_{LT} values and the values of the activation energy obtained from isothermal data is irrelevantly, too.

4. Applications

The criterion for finding the analytical form of $f(\alpha)$ as well as the observations concerning the application of Li and Tang's procedure were checked for:

a. simulated TG curves for a single reaction;

b. simulated TG curves for two consecutive reactions;

c. TG curves obtained by Gotor *et al.* [11] for the thermal dissociation of smithsonite.

4.1. Simulated TG curves for a single reaction

The data were simulated for: $f(\alpha) = 1 - \alpha$; $E = 58.5\, kJ \cdot mol^{-1}$; $A = 900\, s^{-1}$, and for the heating rates: 0.15; 0.5; 1; 3; 5 and 10 $K \cdot min^{-1}$.

In order to estimate the activation energy the isoconversional methods Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Li-Tang were applied. For the use of Flynn-Wall-Ozawa method, the factor 1.052 was corrected according to the first procedure suggested by Flynn [12] (two iterations). The Li and Tang method was applied for $\alpha_1 = 0$; 0.05; 0.1; 0.2 and 0.3. All isoconversional methods gave values of E which practically equal the value used to simulate the TG curves. As was expected, the E value obtained by Li and Tang method does not depend on the value of α_1.

In order to check the suggested criterion to find $f(\alpha)$, the following differential conversion function:

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

with $n = 0.7$; 0.8; 0.9; 1; 1.1; 1.2; 1.3, was considered.

For $\alpha_1 = 0.1$, using relation (5), the values of $\ln A$ were calculated for $0.15 \leq \alpha \leq 0.95$. Fig. 1 shows that $\ln A$ is practically independent on α only for $n = 1$, which corresponds to the differential conversion function used for TG curves simulations.
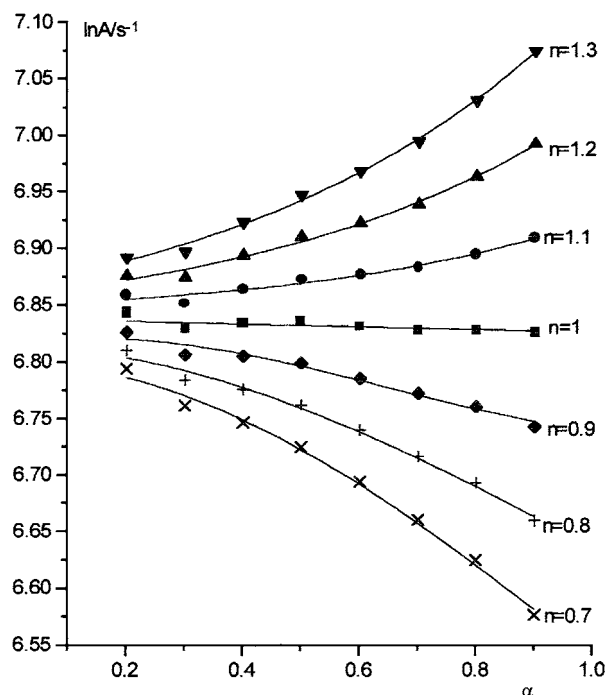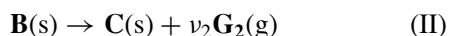
Figure 1 Dependences ln A vs. α for various values of n and $\alpha_1 = 0.1$.

Figure 2 Dependences E vs. α for simulated TG curves corresponding to two consecutive reactions. $T\,E_{FR}$; ● E_{FWO}; ▲ E_{KAS}; ▼ E_{LT} for $\alpha_1 = 0$.
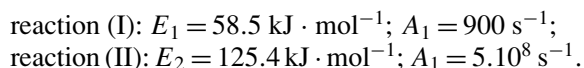
4.2. Simulated TG curves for two consecutive reactions

Let us consider that the solid compound **A** undergoes two decompositions:

$$A(s) \rightarrow B(s) + \nu_1 G_1(g) \qquad (I)$$

$$B(s) \rightarrow C(s) + \nu_2 G_2(g) \qquad (II)$$

where **B** and **C** are solid products, G_1 and G_2 are gaseous products and ν_1 and ν_2 are stoichiometric coefficients.

A reaction order value which equals unity was considered for both (I) and (II) reactions. Let us suppose the following activation parameters values:

reaction (I): $E_1 = 58.5\,\text{kJ}\cdot\text{mol}^{-1}$; $A_1 = 900\,\text{s}^{-1}$;
reaction (II): $E_2 = 125.4\,\text{kJ}\cdot\text{mol}^{-1}$; $A_1 = 5.10^8\,\text{s}^{-1}$.

For simplicity, we supposed that $\nu_1 M_1 = \nu_2 M_2$, where M_1 and M_2 are molecular weights of G_1 and G_2. Under such conditions, the total conversion degree, α, is given by $\alpha = \frac{\alpha_1 + s\alpha_2}{2}$, where α_1 is the conversion degree corresponding to reaction I and α_2—the conversion degree corresponding to reaction II. The procedure for obtaining the TG curves is shown in ref. 10. The TG curves were simulated for the following heating rates: 3; 3.5; 4; 4.5; 5; 6; 7; 8; 10; 12 and 15 K · min^{-1}. For all these heating rates the DTG curves ($\frac{d\alpha}{dT}$ vs. T) exhibits only one maximum. Consequently, a summary analysis of the TG data leads to the conclusion that these correspond to a single reaction. Assuming that the whole process is kinetically described by only one triplet (E, A, $f(\alpha)$), i.e. the rate equation is given by relation (1), the dependence of the apparent activation energy on the conversion degree was determined by help of the mentioned isoconversional methods. From Fig. 2 it turns out that:
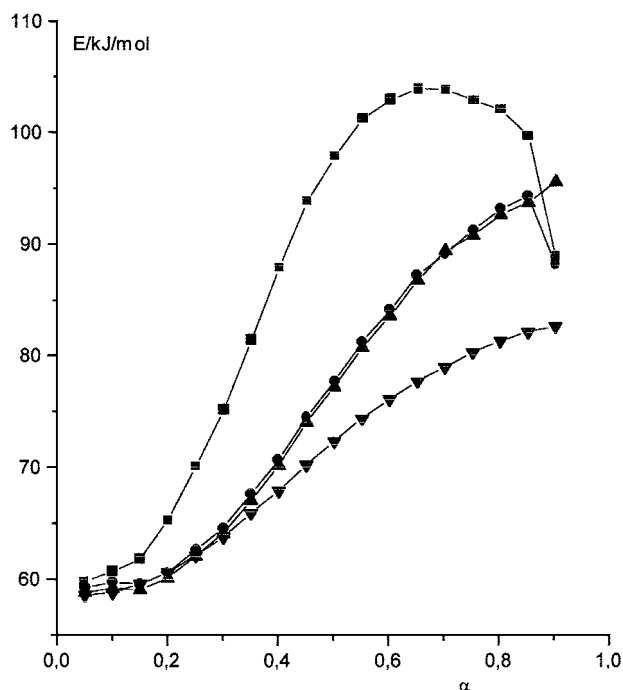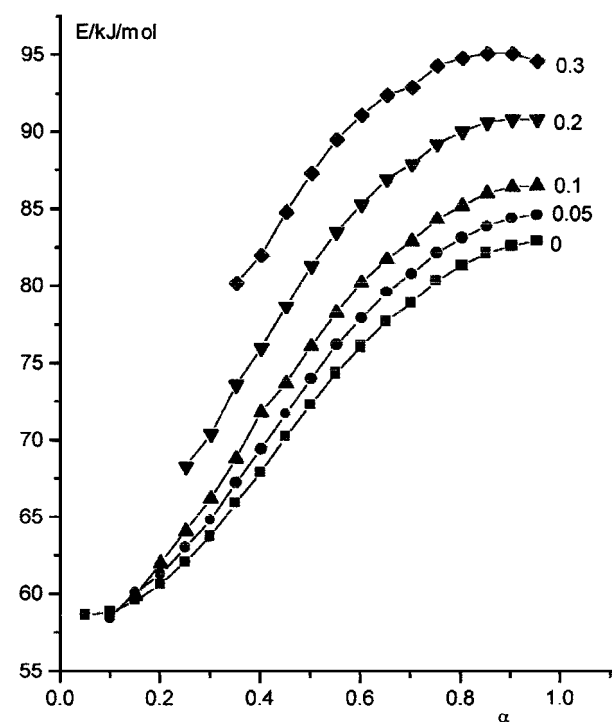

Figure 3 Dependences E_{LT} vs. α for various values α_1 of (simulated TG curves corresponding to two consecutive reactions).

– the values of the apparent activation energy depend on the conversion degree;

– for a given value of α, $E_{FR} > E_{FWO} \approx E_{KAS} > E_{LT}$;

– for $0.25 \leq \alpha \leq 0.80$, the relative deviations of E_{FWO}, E_{KAS} and E_{LT} with respect to E_{FR} are relatively high ($|e\%| > 10\%$).

Fig. 3 shows the dependence E_{LT} vs. α obtained for $\alpha_1 = 0$; 0.05; 0.1; 0.2 and 0,3. As E_{LT} increases with
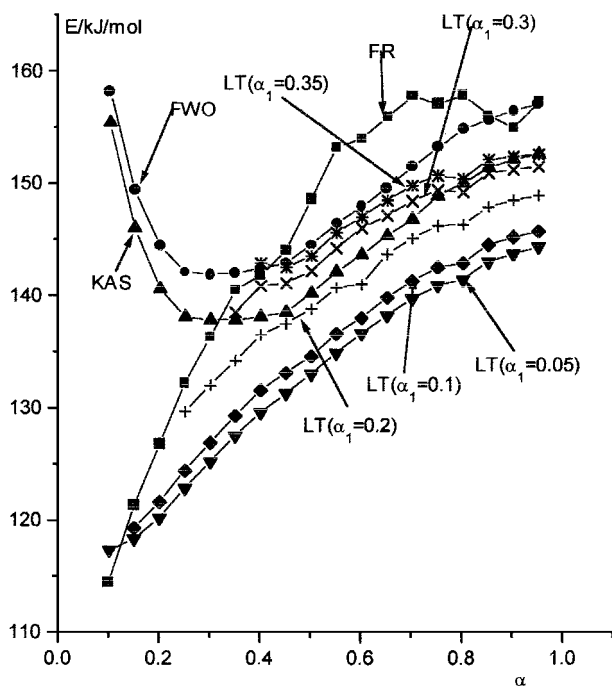
Figure 4 Dependences E vs. α for the thermal decomposition of smithsonite.

α, for a given value of α, E_{LT} increases with α_1. This confirms observations from the previous paragraph.

4.3. TG curves obtained by Gotor *et al.* [11] for the thermal dissociation of smithsonite

The experimental conditions for recording the TG curves corresponding to the thermal dissociation of smithsonite were shown in reference 11. The applied heating rates were 0.12; 0.57; 2.05; 4.11; 6.1 and $8.06 \, \mathrm{K \cdot min^{-1}}$.

Fig. 4 shows the curves $E = E(\alpha)$, for the values of the activation energy estimated by various isoconversional methods.

For the presented data one can see that:

 – for $0.1 \leq \alpha \leq 0.25$, E_{FWO} and E_{KAS} decrease with α, while E_{FR} and E_{LT} increase with α on the whole range of α;

 – for a given value of α, E_{LT} increases with α_1;

 – for a given value of α, the deviations of E_{LT} with respect to E_{FWO}, E_{KAS} and respectively E_{FR} decrease with α_1.

All the applied methods gave acceptable but relatively high errors in E ($\pm 8\%$ - $\pm 9\%$), showing that the investigated process is rather complex.

Removing the rate of $0.12 \, \mathrm{K \cdot min^{-1}}$, we obtained, by all methods, practically the same value of the activation energy ($152.0 \, \mathrm{kJ \cdot mol^{-1}} - 159.5 \, \mathrm{kJ \cdot mol^{-1}}$) which for $\alpha \geq 0.2$ does not depend on the conversion degree. This could be explained either by the change of the reaction mechanism at the transition from $0.12 \, \mathrm{K \cdot min^{-1}}$ to $0.57 \, \mathrm{K \cdot min^{-1}}$, or by the change of mechanism from the relatively low temperatures characteristic for the investigated reaction at $0.12 \, \mathrm{K \cdot min^{-1}}$ at higher tempera-

tures corresponding to $\beta \geq 0.57 \, \mathrm{K \cdot min^{-1}}$. The fact that values close to $E \approx 155 \, \mathrm{kJ \cdot mol^{-1}}$ were obtained using the FWO, KAS, FR and LT (for $\alpha_1 = 0.35$) methods for $\alpha \geq 0.75$ considering all the heating rates suggests that the second explanation is valid. These values of α correspond to $T \geq 680 \, \mathrm{K}$, i.e. $T \approx 680 \, \mathrm{K}$ is the transition temperature from one mechanism to the other one. This interpretation agrees with that given by Gotor *et al.* [11] through analysis of TG and CRTA data.

5. Conclusions

1. It was shown that if the activation energy does not depend on the conversion degree, the isoconversional method suggested by Li and Tang can be used can be used in order to determine the analytical form of the differential conversion function.

2. It was equally shown that in the cases when the activation energy depends on the conversion degree, the values of the activation energy obtained by applying Li and Tang's method depend on the lower limit of the integrals required by it. This is one reason for we consider that this method is not suitable to find the dependence $E = E(\alpha)$.

3. The suggested criterion to obtain the analytical form of $f(\alpha)$ was checked for simulated TG curves corresponding to only one decomposition reaction.

4. For the simulated TG curves corresponding to two consecutive reactions as well as for the TG curves obtained at the investigation of the thermal dissociation of smithsonite, using various isoconversional methods, the dependencies $E = E(\alpha)$ were determined. In such a way, it was checked that if E depends on α, when applying Li and Tang's method the value of the activation energy depends on the lower limit of the integrals required by the method.

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