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KINETIC ANALYSIS OF DISSOCIATION OF SMITHSONITE FROM A SET OF NON-ISOTHERMAL DATA OBTAINED AT DIFFERENT HEATING RATES

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Abstract

The isoconversional methods (Friedman and Flynn–Wall–Ozawa) as well as the invariant kinetic parameters method (IKP) were used in order to work the TG data corresponding to the thermal dissociation of smithsonite. As a result we mention a mechanism change at $T\approx 671$ K. For $T>671$ K, which corresponds to heating rates in the range 0.57– 8.06 K min^{-1}, a reaction order model with $1<n\leq 1.4$ describes the experimental data.

Keywords: invariant kinetic parameters method, isoconversional method, smithsonite, thermal dissociation

Introduction

In a recent article [1], the isothermal, non-isothermal and constant rate thermal analysis (CRTA) were used for discerning the kinetics of the thermal dissociation of smithsonite. It was shown that the mechanism for the thermal decomposition of this compound depends on temperature. For temperatures lower than 650 K an A0.5 kinetic model is approximately valid, whereas at temperatures higher than 690 K the reaction kinetics obeys a F1 kinetic law. As shown in previous papers [2–8], for the analyzed case the TG curves can be relatively correct described for various kinetic models. In many cases among the activation parameters corresponding to each kinetic model, high differences can be noticed. In order to find the true kinetic model from non-isothermal data, the values of the activation parameters obtained for various ki-

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netic models using a single TG curve were compared with those obtained from a single CRTA experiment. The true kinetic model corresponds to a reasonable agreement between the activation parameters evaluated from TG and CRTA curves.

In this work we are going to analyze the TG non-isothermal data [1] obtained for the thermal decomposition of smithsonite, at several linear heating rates. In order to find the kinetic model, two procedures are going to be applied, namely:

– the procedure according to which the true kinetic model corresponds to a good agreement between the value of the activation energy obtained by help of an isoconversional method with that obtained by help of a differential or integral method, for each TG curve [9];

– the IKP method (invariant kinetic parameters) method, proposed by Lesnikovich and Levchik [10, 11] and used by Bourbigot *et al.* in order to investigate the fire-retardancy [12–15], the oxidative degradation of epoxy resins [16, 17] as well as the thermal behaviour of cotton-modacrylic fibre [18].

Experimental

The same batch of mineral zinc carbonate sample characterized in a previous work [1] has been used. It was reported [1] that the sample was constituted by a single phase of smithsonite. The following results were given for the chemical analysis: ZnO, 57.69%; Fe_2O_3, 1.81%; Na_2O, 3.56%; MgO, 0.31%; CaO, 0.19%; SiO_2, 1.20%; others , 0.22%; ignition loss, 35.21%.

A Cahn electrobalance connected to a high vacuum system was used. The TG curves were recorded under a high vacuum. The starting sample mass was selected in such a way that the pressure never exceeded the value of 10^{-4} mbar. It would be expected that under these experimental conditions the maximum decomposition rate would be small enough to minimize the influence of heat and mass transfer phenomena on the forward reaction.

Calculation methods of the kinetic parameters

Isoconversional methods

The isoconversional methods to evaluate the activation energy are advantageous as they do not require the knowledge of the analytical form of conversion function and, on the other hand, they give the possibility to evidence the change of the activation energy with the conversion degree.

Friedman's isoconversional method [19] is based on the equation:

$$\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\ln Af(\alpha)-\frac{E}{RT} \tag{1}$$

where β is the linear heating rate, α – the conversion degree, T – the temperature (K), A – the pre-exponential factor, $f(\alpha)$ – the differential function of conversion, E – the activation energy and R – the gas constant.

For α=const. (isoconversion) the plot of $\ln\beta(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $(1/T)$ for various heating rates should be a straight line, whose slope allows calculating the activation energy.

The method suggested by Ozawa [20] and independently by Flynn and Wall [21] is based on the following equation:

$$\ln\beta \cong \ln\frac{AE}{R} - \ln g(\alpha) - 5.331 - 1.052\frac{E}{RT} \tag{2}$$

where $g(\alpha)=\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}$ is the integral conversion function.

For α=const., using TG curves recorded at various heating rates, one can plot $\ln\beta$ *vs.* $(1/T)$. From the slope of the obtained straight line, the activation energy can be calculated.

In a recent paper [22] we showed that for E independent of α, E_{FR} (activation energy evaluated using Friedman's method) values coincide with E_{FWO} (activation energy evaluated using Flynn–Wall–Ozawa method); if E values change with α, $E_{\mathrm{FR}} \neq E_{\mathrm{FWO}}$. The dependence $E=E(\alpha)$ can be justified considering (a) the complexity of heterogeneous process; (b) the change of the mechanism of the process with the heating rate and (c) the change of the mechanism of the process with the temperature.

If E does not depend on α, in order to determine of $f(\alpha)$, it was suggested [9] the comparison of the E value obtained by help of an isoconversional method with the values obtained using a differential or integral method, which necessitates the knowledge of $f(\alpha)$ (for instance, the Coats–Redfern integral method [23]). Each considered kinetic model leads to a given value of the activation energy. The true kinetic model is that which leads to a value of E which is the closest to that obtained with the help of an isoconversional method.

Invariant kinetic parameters method (IKP)

It is well known that several forms of the conversion function could accurately describe a TG curve; to each form of the conversion function, a given pair of the activation parameters is obtained. In many cases high differences among the activation parameters obtained for each conversion function have to be noticed. This is the reason for the use of a single TG curve in order to determine the kinetic parameters is not recommendable. It was observed [5–8, 24] that the values of the activation parameters, obtained for different expressions of $f(\alpha)$, are correlated through the relation of the compensation effect:

$$\ln A = \alpha^* + \beta^* E \tag{3}$$

where α^* and β^* are constant parameters.

Starting from these observations, Lesnikovich and Levchik [10, 11] worked the *invariant kinetic parameters method* (IKP). In order to apply this method for a given heterogeneous reaction, TG curves for several heating rates (β_v, v=1, 2, 3, …) should be recorded. Besides a set of conversion functions, $f_j(\alpha)$, j=1, 2, 3, …, is considered.

For each heating rate, β_v, using an integral or differential method, the pairs (A_{vj}, E_{vj}) characteristic for each conversion function, are determined. Using the relation of the compensation effect, for each heating rate the corresponding pair of compensation parameters (α^*_v, β^*_v) is determined. The straight lines $\ln A_v$ *vs.* E_v for several heating rates should intersect in a point which corresponds to the true values of A and E. These were called by Lesnikovich and Levchik [10, 11], invariant activation parameters (A_{inv}, E_{inv}). Certain variations of the experimental conditions determine actually a region of intersection in the space A, E. This is the reason for the evaluation of the invariant activation parameters is performed using the relation:

$$\ln A_{inv} = \alpha^*_v + \beta^*_v E_{inv} \tag{4}$$

which leads to:

$$\alpha^*_v = \ln A_{inv} - \beta^*_v E_{inv} \tag{5}$$

Thus, the plot α^*_v *vs.* β^*_v is actually a straight line whose parameters allow evaluating the invariant activation energy and invariant pre-exponential factor. Lesnikovich and Levchik called relation (5) as relation of *supercorrelation*. Also, Lesnikovich and Levchik [10, 11] suggested a statistical method to evaluate the probabilities of the considered kinetic functions.

Results and discussion

Figure 1 shows the TG curves recorded for the thermal decomposition of smithsonite at heating rates ranging from 0.12 to 8.06 K min^{-1}. The corresponding DTG curves were obtained by numerical differentiation of TG curves.

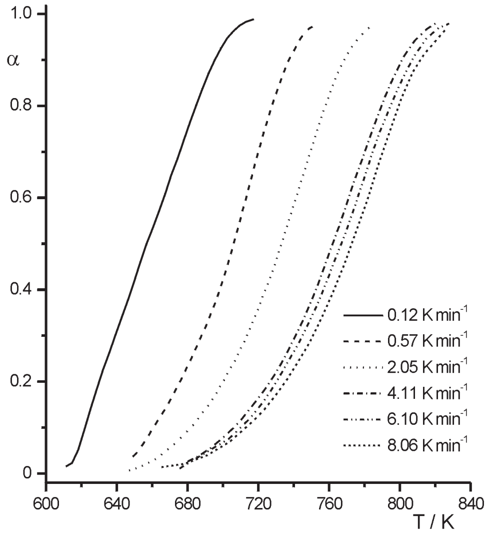

Fig. 1 TG curves recorded at different heating rates

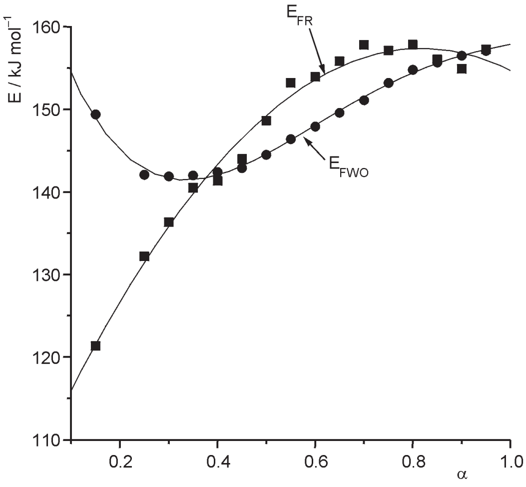

Fig. 2 Dependencies E_{FR} and E_{FWO} on α. 0.12 K min^{-1}≤β≤8.06 K min^{-1}

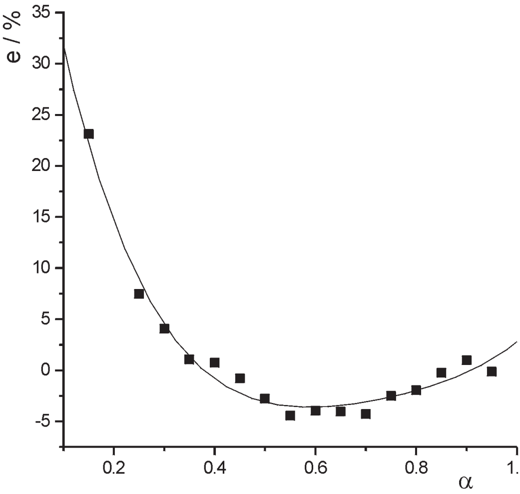

Fig. 3 The dependence $e\% = \frac{E_{FWO} - E_{FR}}{E_{FR}} 100$ *vs.* α for the data from Fig. 1

The E_{FR} and E_{FWO} were evaluated from the data shown in Fig. 1 for values of the conversion degree comprised in the range 0.20–0.95 and for 0.12 K min^{-1}≤β≤ 8.06 K min^{-1}. As seen from Fig. 2, E_{FR} and E_{FWO} depend differently on α. The relative deviation of E_{FWO} with respect to E_{FR}, *e*%, is shown in Fig. 3. According to the obtained results, |*e*%|>10% for α≤0.40. As previously shown [9, 22] if *E* depends on α the Friedman method is recommended. From Fig. 2 it turns out that for 0.65≤α≤0.95, E_{FR} has practically constant values comprised between 154.9(±5.9) and 157.9(±7.9) kJ mol^{-1}. In the same range of α, the values of E_{FWO} coincide practically with the values of E_{FR} (149.6(±6.6) kJ $mol^{-1} \leq E_{FWO} \leq 157.1(\pm 6.4)$ kJ mol^{-1}). From TG curves it turns out that for this range of α, $T\geq671$ K. On the other hand, $T\leq671$ K for $\beta=0.12$ K min^{-1} and $\alpha\leq0.65$, and $T>671$ K for almost all the points of the TG curves recorded at 0.57 K $min^{-1} \leq\beta\leq8.06$ K min^{-1}. Thus it appears that for $T>671$ K the investigated decomposition mechanism is described by a certain $f(\alpha)$ whereas, for $T<671$ K, the mechanism exhibits a complex character, with E changing with α. This conclusion agrees with that resulting from the comparison of the isothermal and non-isothermal data [1], according to which for $T<650$ K and $T>690$ K the smithsonite dissociation occurs according to two different mechanisms, the transition between them being located in the temperature range 650–690 K.

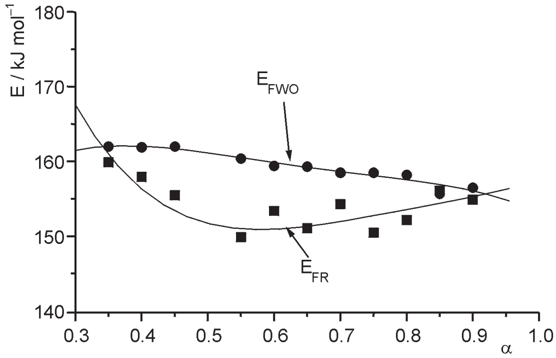

Fig. 4 Dependencies E_{FR} and E_{FWO} on α. $T\geq690$ K

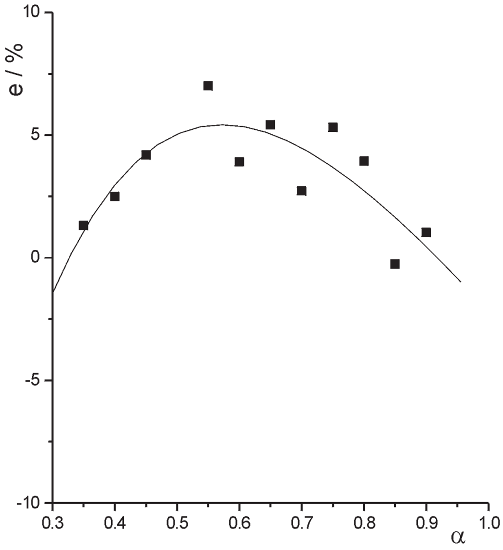

Fig. 5 The dependence $e\% = \frac{E_{FWO}-E_{FR}}{E_{FR}}100$ *vs.* $T\geq690$ K

As seen from Figs 4 and 5, for $T\geq690$ K, E_{FR} and E_{FWO} have close values, e% being comprised in the range –0.26 to 7.00%. The average values of E_{FR} and E_{FWO} are 159.5 and 153.6 kJ mol^{-1}, respectively. The standard deviations of E_{FR} and E_{FWO} are ±7.5 and ±9.7%, respectively. These acceptable but relatively high deviations could be assigned to the fact that for, $T\geq690$ K too, the dissociation of smithsonite occurs according to a complex mechanism, with one mechanism prevailing.

The values of T higher than 690 K corresponds practically to TG curves for $0.57\ \mathrm{K\ min^{-1}}\leq\beta\leq8.06\ \mathrm{K\ min^{-1}}$ (only for $\alpha\geq0.85$, $T\geq690$ K for $\beta=0.12\ \mathrm{K\ min^{-1}}$). This is the reason for we are going to use this range of heating rates in order to analyze the TG data by IKP method. The models considered for IKP method are summarized in Table 1. The reaction order model (Fm) was used for m=1; 1.15; 1.2; 1.3 and 1.4. As far as the Avrami–Erofeev model (An) this was used for n=0.5; 2; 3 and 4. The activation parameters were evaluated by help of Coats–Redfern method for $\approx0.1\leq\alpha\leq\approx0.8$. The activation parameters values are listed in Table 2.

Table 1 Analytical expressions for $f(\alpha)$ and $g(\alpha)$ functions

Symbol	$f(\alpha)$	$g(\alpha)$	
Fm	$(1-\alpha)^m$	$-\ln(1-\alpha)$	for m=1
		$\dfrac{1-(1-\alpha)^{(-m+1)}}{-m+1}$	for $m\neq1$
R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	
R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	
An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$	$[-\ln(1-\alpha)]^{1/n}$	

As expected, for each heating rate the activation parameters are correlated through the compensation effect relationship (Eq. (3)). The compensation effect parameters are listed in Table 3. As α^* and β^* are correlated by the supercorrelation relation (Eq. (5)), one obtains:

$$\ln A_{inv}=18.680(\pm2.094);\ A_{inv}\ \text{expressed in s}^{-1}$$

$$E_{inv}=158.8(\pm12.5)\ \text{kJ mol}^{-1}$$

The E_{inv} value as well as the value of the standard deviation of this quantity is close to the average values of E_{FR} and E_{FWO}, and the standard deviation of the activation energy values determined using isoconversional methods. One has to notice that close values of $\ln A_{inv}$ and E_{inv} are obtained considering only the models F1; A0.5; A2; A3; A4; R2 and R3 ($\ln A_{inv}$=18.052; A_{inv} expressed in s^{-1}; E_{inv}=156.0 kJ mol^{-1}). Obviously, the activation parameters values from Table 2 depend on the considered range of conversion degree. Similar calculation were performed for $\approx0.3\leq\alpha\leq\approx0.9$ (range used for evaluation of E_{FR} and E_{FWO}). The values $\ln A_{inv}$=18.511(±2.433); A_{inv} expressed in s^{-1} and E_{inv}=157.7(±14.5) kJ mol^{-1} were obtained. These are close to those obtained for $\approx0.1\leq\alpha\leq\approx0.8$. Considering the heating rate $\beta=0.12$ K min^{-1} too, for $\approx0.3\leq\alpha\leq\approx0.9$, the values $\ln A_{inv}$=15.545; (A_{inv} expressed in s^{-1}) and E_{inv}=141.0 kJ mol^{-1}

were obtained. The difference between these values and those obtained for 0.57 K min^{-1}≤β≤8.06 K min^{-1} show that the mechanism for β=0.12 K min^{-1} is different. Finally, the relatively high standard deviations of lnA_{inv} and E_{inv} reconfirm the complexity of decomposition mechanism in the range of heating rates 0.57 K min^{-1} ≤β≤8.06 K min^{-1}.

Table 2 Kinetic parameters evaluated from TG curves using Coats–Redfern method

Mechanism	β=0.57 K min^{-1}			β=2.05 K min^{-1}			β=4.11 K min^{-1}			β=6.1 K min^{-1}			β=8.06 K min^{-1}		
	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
F1	145.1	16.376	0.9932	138.4	15.512	0.99979	136.8	14.994	0.99991	136.2	15.154	0.99977	135.6	15.172	0.99944
F1.15	151.4	17.555	0.99914	144.9	16.691	0.99956	142.5	16.000	0.99976	142.0	16.157	0.99963	141.7	16.243	0.99881
F1.2	153.5	17.956	0.99903	147.1	17.092	0.99943	144.4	16.343	0.99967	143.9	16.498	0.99953	143.9	16.608	0.99885
F1.3	157.9	18.773	0.99875	151.6	17.910	0.99911	148.4	17.038	0.99942	147.9	17.191	0.99926	148.2	17.351	0.99795
F1.4	162.3	19.606	0.99838	156.3	18.744	0.99870	152.5	17.748	0.99909	152.0	17.898	0.99889	152.6	18.110	0.99726
R2	125.7	12.731	0.99818	118.4	11.874	0.99873	119.1	11.871	0.99885	118.5	12.038	0.99844	116.7	11.872	0.99967
R3	131.9	13.898	0.99887	124.8	13.037	0.99942	124.8	12.872	0.99948	124.2	13.038	0.99921	122.7	12.926	0.99993
A0.5	301.7	43.458	0.99937	288.8	40.581	0.99980	286.0	38.929	0.99991	284.9	38.871	0.99998	283.8	38.651	0.99947
A2	66.8	2.425	0.99919	63.2	2.561	0.99975	62.2	2.606	0.99981	61.9	2.875	0.99972	61.5	3.011	0.99936
A3	40.7	–2.463	0.99903	38.1	–2.000	0.99970	37.3	–1.770	0.99986	37.1	–1.467	0.99965	36.8	–1.292	0.99927
A4	27.6	–5.045	0.99882	25.6	–4.427	0.99963	24.9	–4.108	0.99982	24.7	–3.789	0.99954	24.5	–3.596	0.99914

The comparison of the activation parameters values listed in Table 2 with the values E_{inv}=158.8 kJ mol^{-1} and lnA_{inv}=18.680 obtained for 0.57 K min^{-1}≤β≤8.06 K min^{-1}, leads to the conclusion that the prevailing mechanism belongs to the group Fm with the highest probability F1.4 for which ln$\overline{A}$=18.421(±0.764) and $\overline{E}$=155.1(±4.4) kJ mol^{-1}.

Table 3 The values of the compensation parameters for the data from Table 2

β/K min^{-1}	α^* A/s^{-1}	β^*/mol kJ^{-1}	r
0.57	–9.478(±0.195)	0.17721(±0.00129)	0.99976
2.05	–8.374(±0.157)	0.17094(±0.00107)	0.99982
4.11	–7.733(±0.198)	0.16505(±0.00139)	0.99968
6.10	–7.356(±0.198)	0.16413(±0.00140)	0.99967
8.06	–7.101(±0.200)	0.16312(±0.00140)	0.99966

The β^* values could be obtained using the relations derived in a previous work [8]:

$$\beta^*_{\mathrm{d}}=\frac{1}{RT}-\frac{\ln\dfrac{f_1(\alpha)}{f_2(\alpha)}}{E_1-E_2} \tag{6}$$

$$\beta^*_{\mathrm{CR}}=\frac{1}{RT}+\frac{1}{E_1-E_2}\ln\frac{E_1 g_1(\alpha)}{E_2 g_2(\alpha)} \tag{7}$$

where T is the temperature corresponding to the conversion degree α, and indexes 1 and 2 correspond to the two considered kinetic models.

Relation (6) results directly from the reaction rate equation and relation (7) results from the Coats–Redfern approximation [23].

The following pairs of kinetic models were considered: F1+A0.5; F1+A2; F1+A3; F1+A4; A0.5+R2; F1.4+A4; F1.4+A2; F1.4+A3 and A0.5+A3. The values of E_1 and E_2 were those determined with the help of Coats–Redfern method (Table 2). Table 4 lists the average values of β^*_{d} and β^*_{R} calculated for $0.1\leq\alpha\leq0.7$ and the pairs of the mentioned kinetic models, and the β^* values obtained from the slopes of the straight lines ln$A$ *vs.* E for all the considered kinetic models. A satisfactory agreement among the values $\overline{\beta^*_{\mathrm{d}}}$, $\overline{\beta^*_{\mathrm{R}}}$ and β^* should be noticed.

Table 4 Values of $\overline{\beta^*_{\mathrm{d}}}$, $\overline{\beta^*_{\mathrm{CR}}}$ and β^* for heating rates in the range 0.57 K min$^{-1}\leq\beta\leq$8.06 K min^{-1}

β/K min^{-1}	$\overline{\beta^*_{\mathrm{d}}}$/mol kJ^{-1}	$\overline{\beta^*_{\mathrm{CR}}}$/mol kJ^{-1}	β^*/mol kJ^{-1}
0.57	0.177(±0.003)	0.179(±0.003)	0.177(±0.001)
2.05	0.171(±0.003)	0.173(±0.004)	0.171(±0.001)
4.11	0.165(±0.003)	0.166(±0.004)	0.165(±0.001)
6.10	0.164(±0.003)	0.166(±0.004)	0.164(±0.001)
8.06	0.163(±0.003)	0.164(±0.004)	0.163(±0.001)

Conclusions

An analysis of the non-isothermal data obtained at the thermal decomposition of smithsonite, processed using (a) isoconversional methods and (b) invariant kinetic parameters method (IKP) was performed.

The use of the isoconversional methods showed that at $T\cong671$ K a change in mechanism occurs. Consequently, the decomposition mechanism at $\beta=0.12$ K min^{-1} differs from the mechanism for $\beta\geq0.57$ K min^{-1}. This result agrees with our previous result [1].

The application of the IKP method for 0.57 K min$^{-1}\leq\beta\leq8.06$ K min^{-1} gave values of the invariant activation parameters close to the values of these parameters obtained for the kinetic model F1.4. It turns out that this is the prevailing kinetic model which characterizes the thermal decomposition of smithsonite at heating rates in the range 0.57 K min$^{-1}\leq\beta\leq8.06$ K min^{-1} (which is equivalent with $T>671$ K). Nevertheless taking into account the high deviations, although acceptable, of the values of the A_{inv} and E_{inv}, it is more correct to say that the prevailing kinetic model belongs to the group Fm with $1\leq m\leq1.4$. This is the reason why we can consider that the results obtained by us are in a satisfactory agreement to those obtained in the previous work [1] concerning the comparison of the values of the activation parameters obtained by using Coats–Redfern method to those obtained using CRTA.

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