

# NON-ISOTHERMAL KINETIC STUDY ON THE DECOMPOSITION OF Zn ACETATE-BASED SOL-GEL PRECURSOR

## Part II. The application of the IKP method

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The paper presents a non-isothermal kinetic study of the decomposition of Zn acetate-based gel precursors for ZnO thin films, based on the thermogravimetric (TG) data. The evaluation of the dependence of the activation energy ( $E$ ) on the mass loss ( $\Delta m$ ) using the isoconversional methods (Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS)) has been presented in a previous paper. It was obtained that the sample dried at 125°C for 8 h exhibits the activation energy independent on the heating rate for the second decomposition step. In this paper the invariant kinetic parameter (IKP) method is used for evaluating the invariant activation parameters, which were used for numerical evaluation of the function of conversion. The value of the invariant activation energy is in a good agreement with those determined by isoconversional methods. In order to determine the kinetic model, IKP method was associated with the criterion of coincidence of the kinetic parameters for all heating rates. Finally, the following kinetic triplet was obtained:  $E=91.7 (\pm 0.1)$  kJ mol<sup>-1</sup>,  $\ln A(s^{-1})=16.174 (\pm 0.020)$  and F1 kinetic model.

**Keywords:** invariant kinetic parameter method, sol-gel, Zn acetate-based precursor

### Introduction

In the first paper from this series [1] the results obtained in the investigation of the non-isothermal decompositions of two Zn acetate-based precursors for ZnO thin films whose preparation differs by the drying temperature (125°C for sample A and 150°C for sample B) were presented. It was pointed out that both samples exhibit three decomposition steps characterized by some specific parameters. The isoconversional methods (Friedman [2], Flynn–Wall–Ozawa [3, 4] and Kissinger–Akahira–Sunose [5]) were used to evaluate the dependencies of the activation energy ( $E$ ) on the mass loss ( $\Delta m$ ). It was obtained that sample A exhibits  $E$  independent on  $\Delta m$  only for the second decomposition step, while the sample B exhibits  $E$  dependent on  $\Delta m$  in all decomposition steps. Consequently, only the second decomposition step of the sample dried at 125°C is characterized by a single kinetic triplet ( $E$ , pre-exponential factor ( $A$ ), function of conversion ( $f(\alpha)$ )). In this paper the invariant kinetic parameters method (IKP method) suggested by Lesnikovich and Levchik [6, 7] will be applied for evaluating the invariant activation parameters of this decomposition step. These parameters will be used for numerical evaluation of the invariant conversion function that is proportional with

the real conversion function. The association of IKP method with the criterion of coincidence of the kinetic parameters for all heating rates [8] will lead to the real kinetic triplet corresponding to the investigated process.

*The invariant kinetic parameters method (IKP method) [6, 7] associated with the criterion of independence of kinetic parameters on the heating rate [8]*

Under non-isothermal conditions, with a linear regime of temperature increase in time ( $\beta=dT/dt=\text{const.}$ , where  $\beta$  is the heating rate,  $T$  – temperature, and  $t$  – time), for a heterogeneous solid-gas reaction, occurring in a single step, the reaction rate is expressed by the known general equation:

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

where:  $\alpha$  is the conversion degree,  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $f(\alpha)$  is the differential conversion function and  $R$  is the gas constant.

The use of Eq. (1) supposes that the kinetic triplet ( $E, A, f(\alpha)$ ) describes the time evolution of a physical or chemical change. Starting from this equation, various methods of the kinetic triplet evaluation were developed.

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Still from 1977, Criado and Morales [9] shown that an  $\alpha$  vs.  $T$  curve, recorded at a certain heating rate, may be relatively correctly described by several kinetic models (expressions of  $f(\alpha)$ ). In many cases [9–23] large differences can be noted among the activation parameters derived from each kinetic model. For a single  $\alpha$  vs.  $T$  curve, the values of the activation parameters, obtained for various analytical forms of  $f(\alpha)$ , are correlated through the relation of the compensation effect (CE):

$$\ln A = a + bE \quad (2)$$

where  $a$  and  $b$  are constant parameters (compensation effect parameters).

Both  $a$  and  $b$  depend on the heating rate and the considered set of the conversion functions [21–23].

Starting with these observations, Lesnikovich and Levchik [6, 7] suggested the invariant kinetic parameters method (IKP method), which can be used for the evaluation of the kinetic triplet from non-isothermal data recorded at several heating rates. In order to apply this method for a given heterogeneous reaction, a set of conversion functions  $f_j, j=1, 3, 3, \dots$ , must be considered. In this paper we will use the following kinetic models: reaction order models (Fn), Avrami-Erofeev models (An), diffusion models (Dn); the expressions of  $f(\alpha)$  corresponding to these models are given in many papers (see for example [8]).

For evaluation of the activation parameters corresponding to a certain pair (kinetic model+heating rate), the integral method suggested by Coats and Redfern (CR method) [24] that is based on relation (3) will be used.

$$\ln \frac{g(\alpha)}{T^2} = \frac{AR}{\beta E} - \frac{E}{RT} \quad (3)$$

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

A plot  $\ln(g(\alpha)/T^2)$  vs.  $1/T$  for a given analytical form of  $g(\alpha)$  should be a straight line of which parameters are  $\ln A$  and  $(-E/R)$ .

IKP method is based on the ‘super-correlation’ relationship, according to which CE parameters are correlated by equation:

$$a_\beta = \ln A_{\text{inv}} - b_\beta E_{\text{inv}} \quad (4)$$

where the index  $\beta$  refers to the heating rate and  $E_{\text{inv}}$  and  $A_{\text{inv}}$  are the invariant activation parameters.

The IKP method can be used for numerical evaluation of  $g_{\text{inv}}(\alpha)$ , by introducing in Eq. (3) the value of the invariant activation parameters. It was pointed out [22, 23] that the values of  $A_{\text{inv}}$  and  $g_{\text{inv}}(\alpha)$  are proportional with the real values of  $A$  and  $g(\alpha)$ . Therefore, IKP method must be associated with the criterion suggested by Perez-Maqueda *et al.* [8] according to which the correct kinetic model correspond to the

**Table 1** Kinetic parameters evaluated by CR method from TG curves corresponding to second decomposition step of the sample dried at 125°C

Model	$\beta=2.5 \text{ K min}^{-1}$			$\beta=5 \text{ K min}^{-1}$			$\beta=7.5 \text{ K min}^{-1}$		
	E/kJ mol <sup>-1</sup>	lnA/s <sup>-1</sup>	-r	E/kJ mol <sup>-1</sup>	lnA/s <sup>-1</sup>	-r	E/kJ mol <sup>-1</sup>	lnA/s <sup>-1</sup>	-r
F1	90.3 (±0.0)	15.79 (±0.01)	0.99999	90.5 (±0.2)	15.89 (±0.43)	0.99919	93.2 (±0.1)	16.54 (±0.01)	0.99993
R2	81.8 (±0.2)	13.40 (±0.04)	0.99926	81.8 (±0.3)	13.51 (±0.08)	0.99680	84.4 (±0.2)	14.19 (±0.04)	0.99920
R3	84.6 (±0.1)	14.18 (±0.03)	0.99969	84.6 (±0.3)	14.28 (±0.07)	0.99779	87.2 (±0.1)	14.95 (±0.03)	0.99962
A0.5	188.4 (±0.0)	40.49 (±0.01)	0.99999	189.0 (±0.3)	40.06 (±0.01)	0.99929	194.4 (±0.1)	40.96 (±0.03)	0.99993
A1.5	57.6 (±0.0)	7.35 (±0.00)	0.99999	57.7 (±0.1)	7.63 (±0.03)	0.99908	59.4 (±0.0)	8.20 (±0.01)	0.99993
A2	41.3 (±0.0)	3.02 (±0.00)	0.99999	41.3 (±0.1)	3.39 (±0.00)	0.99896	42.5 (±0.0)	3.92 (±0.01)	0.99992
A2.5	31.5 (±0.0)	0.35 (±0.00)	0.99999	31.4 (±0.1)	0.77 (±0.02)	0.99881	32.4 (±0.0)	1.28 (±0.00)	0.99991
A3	24.9 (±0.0)	-1.48 (±0.00)	0.99999	24.8 (±0.0)	-1.03 (±0.02)	0.99863	25.6 (±0.0)	-0.54 (±0.00)	0.99991
D2	166.0 (±0.4)	33.63 (±0.10)	0.99876	166.0 (±0.7)	33.18 (±0.18)	0.99598	171.2 (±0.4)	34.14 (±0.10)	0.99869
D3	177.0 (±0.2)	35.15 (±0.05)	0.99973	177.3 (±0.5)	34.71 (±0.13)	0.99803	182.6 (±0.2)	35.65 (±0.05)	0.99967
D4	169.7 (±0.3)	33.13 (±0.09)	0.99917	169.7 (±0.6)	32.68 (±0.16)	0.99677	175.0 (±0.3)	33.64 (±0.09)	0.99911

independence of the activation parameters on the heating rate.

So, if the Coats–Redfern equation written in the form:

$$\ln \frac{\beta g(\alpha)}{T^2} = \ln \frac{AR}{E} - \frac{E}{RT} \quad (5)$$

is used, for the correct conversion function, the points  $\{\ln[\beta g(\alpha)/T^2], 1/T\}$  corresponding to all the heating rates lie on the same straight line.

#### Evaluation of the kinetic triplet for the second decomposition step of sample A

Table 1 lists the values of the activation parameters evaluated by CE method and obtained for different kinetic models and heating rates. The calculations were performed for the  $\alpha$  range  $0.05 \leq \alpha \leq 0.75$  in which the relative standard deviations of  $E$  evaluated by isoconversional methods are lower than  $\pm 10\%$ .

For the considered kinetic models, the straight lines corresponding to the CR method are characterized by correlation coefficients with values close to unity. The values of the activation parameters depend on the kinetic model as well as on the heating rate. The differences between the activation parameters corresponding to the considered models are very high. Thus, using statistic criterion one cannot say which model is the real one. Moreover for experimental data affected by experimental errors, the mentioned criterion cannot be applied. For such cases a  $r$  value lower than  $r_{\max}$  could correspond to the true kinetic model. In order to determine the analytical form of  $f(\alpha)$ , in a previous paper [25] we suggested the criterion according to which the true analytical form of the conversion function corresponds to the activation energy determined from a single  $\alpha = \alpha(T)$  curve that equals the activation energy obtained by means of isoconversional methods. By applying this criterion for the analyzed data,  $f(\alpha) = 1 - \alpha$  could be the real kinetic model.

As expected, for each heating rate the activation parameters are correlated through the CE relationship (Eq. (2)). The compensation effect parameters are

listed in Table 2. As  $a$  and  $b$  are correlated by super-correlation relation (Eq. (4)) one obtains:

- for Fn+An models:  $A_{\text{inv}}(\text{s}^{-1}) = 17.04 (\pm 0.43)$ ;  $E_{\text{inv}} = 96.1 (\pm 1.7) \text{ kJ mol}^{-1}$  with  $r = 0.99984$ ;
- for Fn+An+Dn models:  $A_{\text{inv}}(\text{s}^{-1}) = 17.23 (\pm 0.13)$ ;  $E_{\text{inv}} = 99.2 (\pm 10.6) \text{ kJ mol}^{-1}$  with  $r = 0.99998$ .

Thus, the value of  $E_{\text{inv}}$  practically equals the values of the activation energy obtained by means of the isoconversional methods (see the first paper from this series [1]).

The invariant values of the activation parameters for Fn+An kinetic models were used for evaluating  $g_{\text{inv}}(\alpha)$  (Eq. (3) was applied). As shown in Fig. 1, for all the heating rates, the curve  $g(\alpha)$  vs.  $\alpha$  exhibits the same shape, with low differences among the  $g_{\text{inv}}(\alpha)$  values for a given  $\alpha$ . The scattering of results from Fig. 1 is due to the standard deviation of the invariant activation parameters.

Applying Perez-Maqueda *et al.* criterion [8], a single straight line  $\{\ln[\beta g(\alpha)/T^2], 1/T\}$  is obtained for all heating rates only for the kinetic model F1 (Figs 2 and 3). From the parameters of the straight line shown in Fig. 2, one obtains:  $E = 91.7 (\pm 0.1) \text{ kJ mol}^{-1}$  and  $\ln A (\text{s}^{-1}) = 16.17 (\pm 0.02)$ .

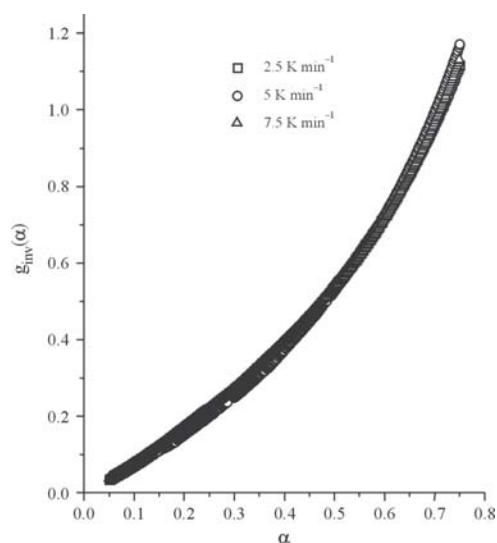
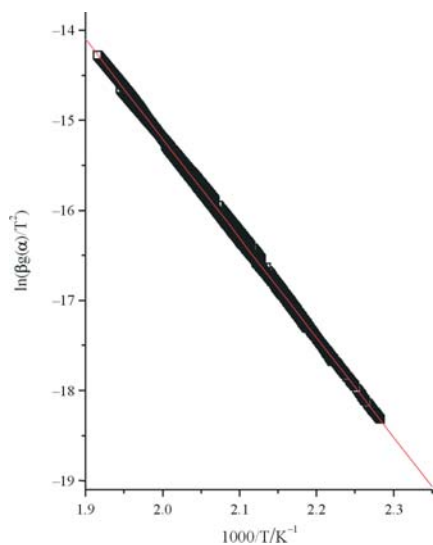


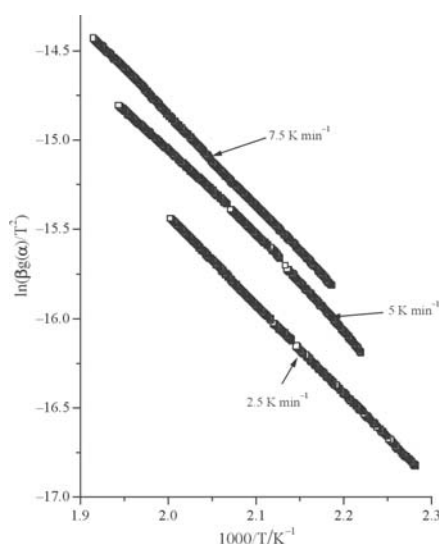
Fig. 1 Dependence of  $g_{\text{inv}}(\alpha)$  on  $\alpha$ , established using invariant activation parameters, for the second decomposition step of the sample dried at  $125^\circ\text{C}$

Table 2 Values of the compensation effect parameters obtained by using the data listed in Table 1

$\beta/\text{K min}^{-1}$	Fn+An models			Fn+An+Dn models		
	$-a$ $\text{A/s}^{-1}$	$b$ $\text{mol kJ}^{-1}$	$r$	$-a$ $\text{A/s}^{-1}$	$b$ $\text{mol kJ}^{-1}$	$r$
2.5	$-7.584 (\pm 0.125)$	$0.2561 (\pm 0.0014)$	0.99991	$-6.978 (\pm 0.505)$	$0.2441 (\pm 0.0043)$	0.99861
5	$-6.945 (\pm 0.126)$	$0.2496 (\pm 0.0014)$	0.99991	$-6.342 (\pm 0.506)$	$0.2377 (\pm 0.0043)$	0.99853
7.5	$-6.543 (\pm 0.126)$	$0.2452 (\pm 0.0014)$	0.99991	$-5.938 (\pm 0.505)$	$0.2337 (\pm 0.0042)$	0.99857



**Fig. 2** Dependence of  $\ln\beta(g(\alpha)/T^2)$  vs.  $1/T$  for F1 kinetic model and the second decomposition step of the sample dried at 125°C



**Fig. 3** Dependence of  $\ln\beta(g(\alpha)/T^2)$  vs.  $1/T$  for A2 kinetic model and the second decomposition step of the sample dried at 125°C

## Conclusions

The application of the isoconversional methods for the non-isothermal decomposition of Zn acetate-based precursors for ZnO thin films, dried at 125 and 150°C, showed [1] that only the second decomposition step of the sample dried at 125°C exhibits  $E$  independent on  $\alpha$ . For this process the invariant kinetic parameter (IKP) method associated with the criterion of independence of kinetic parameters on heating rate leads to the following kinetic triplet:  $E=91.7 (\pm 0.1)$  kJ mol<sup>-1</sup>,  $\ln A(s^{-1})=16.17 (\pm 0.02)$  and  $f(\alpha)=1-\alpha$ .

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