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THE KISSINGER LAW AND THE IKP METHOD FOR EVALUATING THE NON-ISOTHERMAL KINETIC PARAMETERS

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The following problems concerning the apparent compensation effect (CE) ($\ln A=a+bE$, where A is the pre-exponential factor, E is the activation energy, a and b are CE parameters) due to the change of the conversion function and on which the invariant kinetic parameters method (IKP method) is based, are discussed: (1) the explanation of this kind of CE; (2) the choice of the set of conversion functions that checks CE relationship; (3) the dependencies of CE parameters on the heating rate and the temperature corresponding to the maximum reaction rate. Using the condition of maximum of the reaction rate suggested by Kissinger (Kissinger law), it is pointed out that, for a certain heating rate, the CE relationship is checked only for reaction order (Fn) and Avrami–Erofeev (An) kinetic models, and not for diffusion kinetic models (Dn). Consequently, IKP method, which is based on the supercorrelation relationship between CE parameters, can be applied only for the set Fn+An of kinetic models.

The dependencies of a and b parameters on the heating rate and T_m (temperature corresponding to maximum reaction rate) are derived.

The theoretical results are discussed and checked for (a) TG simulated data for a single first order reaction; (b) TG data for PVC degradation; (b) the dehydration of $CaC_2O_4\cdot H_2O$.

Keywords: *apparent compensation effect, IKP method, Kissinger law, non-isothermal kinetic parameters*

Introduction

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

$$\frac{d\alpha}{dt}=\beta\frac{d\alpha}{dT}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α 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. Some relative recent papers [1–14] contain critical analyses of these methods.

Still from 1977, Criado and Morales [15] shown that an α *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 [7, 15–24] large differences can be noted among the activation parameters derived from each kinetic model. For a single α *vs.* T curve, the values of the activation parameters, obtained for various analytical forms of $f(\alpha)$, are correlated through the relation of the apparent compensation effect (CE):

$$\ln A=a+bE \tag{2}$$

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

According to Vyazovkin and Linert [19], Eq. (2) corresponds to a ‘false’ (artificial) compensation effect. The literature data discussed in this paper show that such of CE is inherent to non-isothermal data alone.

Both a and b depend on the heating rate and the considered set of the conversion functions [20–27].

Starting with these observations, Lesnikovich and Levchik [28, 29] 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. IKP method is based on the ‘supercorrelation’ relationship, according to which the CE parameters are correlated by equation:

$$a_\beta=\ln A_{inv}-b_\beta E_{inv} \tag{3}$$

where the index β refers to the heating rate and E_{inv} and A_{inv} are the invariant activation parameters.

In comparison with other methods for evaluation of kinetic parameters from non-isothermal data, the IKP method involves many calculations. This could explain why this method is rarely used. However, the

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IKP method is the single one that associated with the criterion of independence of kinetic parameters on heating rate [30], can be used for finding the true kinetic model without their choice from a pre-established set of $f(\alpha)$ [14]. This very important advantage determines us to investigate the following problems concerning the relations that ground the IKP method:

- the cause of the existence of CE for non-isothermal data and the physical meaning of CE parameters
- the explanation of the dependence of CE parameters on the heating rate, and the considered set of kinetic models

Nicolaev *et al.* [31] explained the existence of CE for a number of chemical reactions taking place in non-isothermal conditions, starting from the Kissinger condition of the reaction rate maximum [32] (Kissinger law). It was pointed out that *a* and *b* parameters depend on both the heating rate and the temperature corresponding to the maximum reaction rate (T_m).

Recently, Mianowski [33] discussed the case of the apparent CE that arises when varying the reaction model. Using the Kissinger law, Mianowski [33] showed that ln*A* and *E* are correlated through relationship (2) when $\delta_m=-([\mathrm{d}\ln f(\alpha_m)/\mathrm{d}\alpha_m]\approx 1$ (the index *m* refers to the maximum reaction rate). For this case, the following relations of *a* and *b* were derived:

$$a=\ln\frac{\beta E}{RT_m^2} \qquad (4)$$

$$b=\frac{1}{RT_m} \qquad (5)$$

which show that CE parameters depend on the heating rate, directly by β and indirectly by T_m.

In this paper, starting with Kissinger law, the validity of apparent compensation effect relationship for the main kinetic models characteristic for heterogeneous processes (reaction order models (Fn), Avrami–Erofeev models (An), diffusion models (Dn)) will be discussed. Two new relations of dependence of the CE parameters on β will be derived. It will be put in evidence the importance of the correct choice of the set of the kinetic models when IKP method is used for the evaluation of non-isothermal kinetic parameters. The theoretical results will be checked and discussed for three sets of non-isothermal data, namely (a) TG simulated data for a single first order reaction; (b) TG data for PVC degradation; (c) TG data for dehydration of $CaC_2O_4\cdot H_2O$.

Theoretical part

The Kissinger law [32] comes from the following condition of maximum of the reaction rate:

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}=0 \quad \text{for } T=T_m \qquad (6)$$

Applying this condition for the rate equation (Eq. (1)), we obtain:

$$\ln A=\ln\frac{\beta E}{RT_m^2}-\ln\delta_m+\frac{E}{RT_m} \qquad (7)$$

which is the logarithmic form of the Kissinger law. In this equation:

$$\delta_m=-\frac{d\ln f(\alpha_m)}{\mathrm{d}\alpha_m} \qquad (8)$$

Mianowski [32] pointed out that δ_m depends on the kinetic model (Table 1 [30] lists the expressions of the main differential and integral conversion functions operating in the heterogeneous reactions). For $E/RT_m\to\infty$, it was obtained that $\delta_m\to 1$ for Fn and An kinetic models, and $\delta_m\neq 1$ for the diffusion kinetic models (Dn). Consequently, only for Fn and An models $\ln\delta_m=0$ and the Eq. (7) becomes:

$$\ln A=\ln\frac{\beta E}{RT_m^2}+\frac{1}{RT_m}E \qquad (9)$$

The last equation was also derived by Nicolaev *et al.* [31] assuming that the main reaction occurs around T_m, $f(\alpha)=(1-\alpha)^n$ and $E/RT_m\to\infty$.

It results that, for a certain heating rate, CE relationship (Eq. (2)) is checked only for Fn and An kinetic models and is not valid for Dn kinetic models. The dependence of δ_m on the diffusion model suggests writing the Eq. (7) as:

$$\ln A_D\equiv\ln A+\ln\delta_m=\ln\frac{\beta E}{RT_m^2}+\frac{1}{RT_m}E \qquad (10)$$

Consequently, for Dn kinetic models, CE relationship is:

$$\ln A_D=\ln A+\ln\delta_m=a^*+b^*E \qquad (11)$$

In the above discussion the limit case $E/RT_m\to\infty$ was considered. But in the real cases of the heterogeneous non-isothermal reactions E/RT_m has finite values (frequently, $E/RT_m\geq 20$). For evaluation of the dependence of $\ln\delta_m$ on E/RT_m, the following relation derived by Gao *et al.* [34] will be used:

$$1-\delta_m g(\alpha_m)=\frac{2RT_m}{E} \qquad (12)$$

where

$$g(\alpha_m)=\int_0^{\alpha_m}\frac{\mathrm{d}\alpha}{f(\alpha)}$$

is the integral conversion function for $\alpha=\alpha_m$.

Table 1 Expressions for $f(\alpha)$ and $g(\alpha)$ functions for the most common mechanisms operating in the heterogeneous reactions [31]

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$*
Reaction order model	Fn**	$(1-\alpha)^n$	$-\ln(1-\alpha)$, for $n=1$ $\frac{1-(1-\alpha)^{(-n+1)}}{-n+1}$, for $n\neq1$
Random nucleation and growth of nuclei (Avrami–Erofeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$	$[-\ln(1-\alpha)]^{1/n}$
One-dimensional diffusion (parabolic law)	D1	$\frac{1}{2\alpha}$	α^2
Two-dimensional diffusion (bidimensional particle shape)	D2	$\frac{1}{[-\ln(1-\alpha)]}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (tridimensional particle shape) Jander equation	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{2/3}]}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (tridimensional particle shape) Ginstein–Brouhnstein equation	D4	$\frac{3}{2[(1-\alpha)^{-1/3}-1]}$	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$

$*g(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}$ is the integral conversion function, $**n=1/2$ corresponds to phase boundary controlled reaction (contracting area, i.e. bidimensional shape) (R2 model) and $n=2/3$ – to phase boundary controlled reaction (contracting volume, i.e. tridimensional shape) (R3 model)

This relation is valid for all kinetic models describing the non-isothermal heterogeneous processes, excepting D1 model for which $\alpha_{\mathrm{m}}=1$ and $\delta_{\mathrm{m}}=0.5$.

For each kinetic model, the calculated dependence of α_{m} on E/RT_{m} was used to evaluate the $\ln\delta_{\mathrm{m}}$ *vs.* E/RT_{m}. Figures 1 and 2 show these dependencies for some kinetic models.

For Fn and An kinetic models, $\ln\delta_{\mathrm{m}}\to0$ when $E/RT_{\mathrm{m}}\to\infty$, and when $E/RT_{\mathrm{m}}\geq20$, $|\ln\delta_{\mathrm{m}}|$ is lower than the usual errors of ln*A* evaluation. Consequently, for these kinetic models, the relation (9) explains the existence of the apparent compensation effect due to the change of the conversion function.

On the other hand, for the diffusion kinetic models D2, D3 and D4, $\ln\delta_{\mathrm{m}}$ increases asymptotically to a constant value (Fig. 2) that is specific for each kinetic model. For the range of α_{m} determined by Gao *et al.* [34], the $\ln\delta_{\mathrm{m}}$ values corresponding to D2, D3 and D4 kinetic models are practically constant ($\overline{\ln\delta_{\mathrm{m}}(\mathrm{D2})}=0.649\pm0.002$; $\overline{\ln\delta_{\mathrm{m}}(\mathrm{D3})}=2.296\pm0.082$; $\overline{\ln\delta_{\mathrm{m}}(\mathrm{D4})}=2.231\pm0.047$). Therefore, for these kinetic models and a given heating rate, $\ln A_{\mathrm{D}}\equiv\ln A+\ln\delta_{\mathrm{m}}$ *vs.* *E* is a straight line.

These theoretical results explain the following statements put in evidence when IKP method was ap-

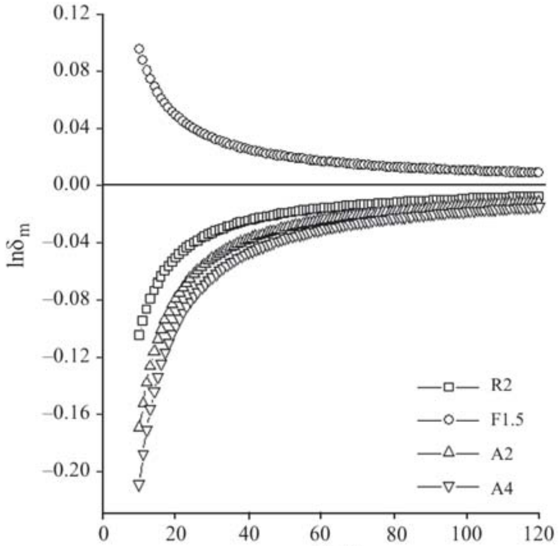

Fig. 1 Curves $\ln\delta_{\mathrm{m}}$ *vs.* E/RT_{m} for the kinetic models R2, F1, F1.5, A2 and A4

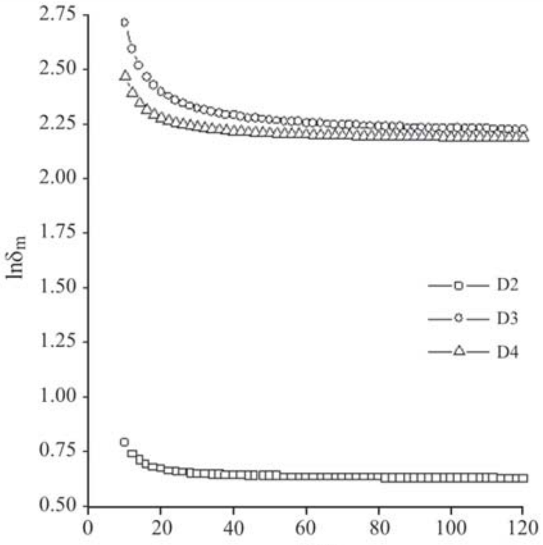

Fig. 2 Curves $\ln\delta_{\mathrm{m}}$ *vs.* E/RT_{m} for the kinetic diffusion models D2, D3 and D4

plied for simulated data [14, 26] and for PVC non-isothermal degradation [27]:

- the standard deviations of a and b values are minimal for the sets consisting from Fn and/or An kinetic models
- the including of Dn kinetic models into a set containing Fn and/or An kinetic models determines the increase of the standard deviations of a and b parameters
- for the set Dn, the standard deviations of E_{inv} and $\ln A_{\mathrm{inv}}$ are significantly higher than those corresponding to other sets of kinetic models, which do not contain Dn kinetic models

The following expressions of CE parameters results from Eqs (2) and (9):

$$b=\frac{\partial \ln A}{\partial E}=\frac{1}{RT_{\mathrm{m}}}+\frac{1}{E}-\frac{\mathrm{d}\ln\delta_m}{\mathrm{d}E}\approx$$

$$\approx\frac{1}{RT}\left(1-\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}\left(\frac{E}{RT_{\mathrm{m}}}\right)}\right)+\overline{\left(\frac{1}{E}\right)} \tag{13}$$

$$a=\ln\beta+\ln E-\ln RT_{\mathrm{m}}^2-1-\left(\ln\delta_{\mathrm{m}}-\frac{E}{RT_{\mathrm{m}}}\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}\left(\frac{E}{RT_{\mathrm{m}}}\right)}\right)\approx$$

$$\approx\ln\beta+\overline{\ln E}-\ln RT_{\mathrm{m}}^2-1-\left(\ln\delta_{\mathrm{m}}-\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}\left(\frac{E}{RT_{\mathrm{m}}}\right)}\right) \tag{14}$$

where the average values of $(1/E)$ and $\ln E$ are evaluated for the considered Fn and An kinetic models. As it will be shown below for some non-isothermal data, the standard deviations of $\overline{\ln E}$ and $\overline{(1/E)}$ are relatively low in comparison with a and b values, respectively.

Table 2 lists the values of

$$\Delta a=\left(\ln\delta_{\mathrm{m}}-\frac{E}{RT_{\mathrm{m}}}\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}\left(\frac{E}{RT_{\mathrm{m}}}\right)}\right)$$

and

$$\Delta b=\left(1-\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}\left(\frac{E}{RT_{\mathrm{m}}}\right)}\right)$$

corresponding to some kinetic models and some values of E/RT_{m}. One can note that, for all kinetic models, an increase of E/RT_{m} determines the increase of $|\Delta a|$ and $|\Delta b-1|$ (for $E/RT_{\mathrm{m}}\to\infty$, $|\Delta a|\to 0$ and $|\Delta b-1|\to 0$). For the kinetic models Fn and An and $E/RT_{\mathrm{m}}\geq 20$ (the most frequently cases), the values of Δa are in the range of the errors in a evaluation, and the introduction of Δb factor in relation (13) does not lead to a significant change of b values. Therefore, we will consider the following approximate relations of a and b:

$$a\approx\ln\beta+\overline{\ln E}-\ln RT_{\mathrm{m}}^2-1 \tag{15}$$

$$b\approx\frac{1}{RT_{\mathrm{m}}}+\overline{\left(\frac{1}{E}\right)} \tag{16}$$

In comparison with the relations derived by Mianowski (Eqs (4) and (5)), these expressions of a and b contain some supplementary terms.

Table 2 The values of $\Delta a=\{\ln\delta_{\mathrm{m}}-(E/RT_{\mathrm{m}})(\mathrm{d}\ln\delta_{\mathrm{m}})/[\mathrm{d}(E/RT_{\mathrm{m}})]\}$ and $\Delta b=\{1-(\mathrm{d}\ln\delta_{\mathrm{m}})/[\mathrm{d}(E/RT_{\mathrm{m}})]\}$ corresponding to some kinetic models and three values of E/RT_{m}

Kinetic model	$E/RT_{\mathrm{m}}=10$		$E/RT_{\mathrm{m}}=20$		$E/RT_{\mathrm{m}}=30$	
	Δa	Δb	Δa	Δb	Δa	Δb
R2	–0.2059	0.9899	–0.1040	0.9974	–0.0684	0.9999
R3	–0.1337	0.9935	–0.0685	0.9983	–0.0452	0.9992
F1	0	1	0	1	0	1
F1.5	0.1783	1.0083	0.0965	1.0024	0.0650	1.0011
A2	–0.3449	0.9826	–0.1647	0.9958	–0.1062	0.9982
A3	–0.4033	0.9797	–0.1939	0.9950	–0.1253	0.9979
A4	–0.4231	0.9787	–0.2040	0.9948	–0.1319	0.9978
D1	–0.6931	1	–0.6931	1	–0.6931	1
D2	1.0515	1.0259	0.7480	1.0037	0.6888	1.0012
D3	3.3058	1.0596	2.6498	1.0125	2.4676	1.0048
D4	2.8466	1.0379	2.4166	1.0069	2.3127	1.0025

Applications

The theoretical results will be checked and discussed for three sets of non-isothermal data, namely (a) TG simulated data for a single first order reaction; (b) TG data for PVC degradation; (c) TG data for dehydration of $CaC_2O_4 \cdot H_2O$.

For each set of non-isothermal data, the compensation effect parameters *a* and *b* (Eq. (2)) and *a** and *b** (Eq. (11)) were evaluated from the parameters of the straight lines ln*A* *vs.* *E* and (ln*A*+lnδ_m) *vs.* *E*, respectively. In these calculations we will consider the following sets of the kinetic models: Fn+An; Dn^t (D1, D2, D3 and D4); Dn (D2, D3 and D4); Fn+Dn+Dn^t; Fn+An+Dn. For evaluation of *a** and *b** (Eq. (11)) we will consider that $\ln\delta_m \approx 0$ for Fn and An kinetic models and $\ln\delta_m$(D1)=–0.693; $\overline{\ln\delta_m}$(D2)=0.649; $\overline{\ln\delta_m}$(D3)=2.296; $\overline{\ln\delta_m}$(D4)=2.231.

The correctness of the relations (15) and (16) will be checked by comparing the values of *a* and *b* calculated using these relations with those determined from the parameters of the straight lines ln*A* *vs.* *E* plotted for the set Fn+An.

The invariant activation parameters will be evaluated by IKP method applied for the parameters of the straight lines ln*A* *vs.* *E* and lnA_D *vs.* *E*, and the CE parameters calculated using Eqs (15) and (16).

Simulated TG curves for a single reaction

The non-isothermal simulated data, which unlike the experimental data are not affected by noises, were analyzed. The simulated data for $f(\alpha)=1-\alpha$, $E=167$ kJ mol^{-1}, $A=1.6\cdot10^6$ s^{-1} and the heating rates 2, 5, 10 and 15 K min^{-1} were calculated by Perez-Maqueda *et al.* [30] through numeric integration of the reaction rate equation, using Runge–Kutta procedure in the Mathcad software with an error in calculation lower than 10^{-5}%.

For the application of the IKP method, the following functions of conversion were used: Fn for *n*=1/2 (R2 model), 2/3 (R3 model), 0.8, 1.2, 1.5 and 2; An for *n*=1.5, 2.0, 2.5, 3.0 and 4.0; and Dn for *n*=1, 2, 3 and 4. The evaluation of the activation parameters corresponding to each conversion function and heating rate was performed by the differential method (method D) based on Eq. (1) written in the form:

$$\ln\beta\frac{d\alpha}{dT} - \ln f(\alpha) = \ln A - \frac{E}{RT} \qquad (17)$$

The plots lnβ(dα/d*T*)–ln*f*(α) *vs.* (1/*T*) for a given analytical form of *f*(α) should be a straight line whose parameters are ln*A* and (–*E*/*R*).

In Figs 3a and b the curves ln*A* *vs.* *E* and (ln*A*+lnδ_m) *vs.* *E* for β=2 K min^{-1} are shown. Similar curves were obtained for all heating rates. The inspection of these curves shows: (1) for Fn and An kinetic models that exhibit $\ln\delta_m \approx 0$, ln*A* *vs.* *E* is a straight line; (2) the plots ln*A* *vs.* *E* for Dn kinetic models are not on the straight line corresponding to Fn+An kinetic models; (3) (ln*A*+lnδ_m) *vs.* *E* is a straight line for Dn kinetic models with parameters different than those for Fn+An kinetic models. These results are in agreement with our theoretical considerations according to which: (1) for Fn+An kinetic models ln*A* *vs.* *E* is a straight line, while for Dn kinetic models a straight line is obtained only for (ln*A*+lnδ_m) *vs.* *E*; (2) the dependence of lnδ_m on the diffusion kinetic model explains why the parameters of the (ln*A*+lnδ_m) *vs.* *E* straight lines corresponding to Fn+An kinetic models and Dn kinetic models have different values.

The values of the CE parameters *a* and *b* (from Eq. (2)) and *a** and *b** (from Eq. (11)) are listed in Tables 3 and 4, respectively. The inspection of these Tables shows that: (1) the standard deviations of *a* and *b*

Table 3 Values of the compensation effect parameters *a* and *b* (Eq. (2)) for the TG simulated data and the considered sets of the kinetic models

β/ K min^{-1}	Set Fn+An			Set Dn^t			Set Dn		
	–*a*	*b*	*r*	–*a*	*b*	*r*	–*a*	*b*	*r*
2	8.57±0.05	0.1370±0.0003	1	5.79±1.62	0.1159±0.0068	0.9966	5.68±4.64	0.1154±0.0181	0.9880
5	7.73±0.05	0.1319±0.0003	1	4.93±1.62	0.1108±0.0068	0.9963	4.88±4.64	0.1105±0.0179	0.9871
10	7.09±0.05	0.1281±0.0003	1	4.45±1.60	0.1072±0.0067	0.9961	4.22±4.59	0.1067±0.0179	0.9862
15	6.71±0.05	0.1259±0.0003	1	3.93±1.62	0.1047±0.0068	0.9958	3.93±4.53	0.1047±0.0177	0.9860

β/ K min^{-1}	Set Fn+An+Dn^t			Set Fn+An+Dn		
	–*a*	*b*	*r*	–*a*	*b*	*r*
2	7.89±0.49	0.1292±0.0028	0.9968	7.88±0.51	0.1292±0.0029	0.9968
5	7.05±0.49	0.1241±0.0028	0.9965	7.04±0.51	0.1242±0.0029	0.9965
10	6.42±0.49	0.1203±0.0028	0.9963	6.41±0.51	0.1204±0.0029	0.9963
15	6.06±0.49	0.1182±0.0028	0.9962	6.05±0.51	0.1182±0.0029	0.9962

Table 4 Values of the compensation effect parameters a^* and b^* (Eq. (11)) for the TG simulated data and the considered sets of the kinetic models

β/K min^{-1}	Set Dn^t			Set Dn		
	$-a$	b	r	$-a$	b	r
2	11.25±0.52	0.1439±0.0022	0.9998	9.96±0.12	0.1390±0.0005	1
5	10.41±0.54	0.1389±0.0022	0.9997	9.10±0.13	0.1339±0.0005	1
10	9.75±0.51	0.1350±0.0021	0.9998	8.48±0.12	0.1301±0.0005	1
15	9.40±0.55	0.1328±0.0023	0.9997	8.07±0.13	0.1278±0.0005	1

β/K min^{-1}	Set Fn+An+Dn^t			Set Fn+An+Dn		
	$-a$	b	r	$-a$	b	r
2	8.42±0.25	0.1343±0.0014	0.9992	8.37±0.17	0.1345±0.0010	0.9997
5	7.58±0.25	0.1293±0.0014	0.9991	7.53±0.17	0.1295±0.0010	0.9996
10	6.94±0.25	0.1255±0.0014	0.9991	6.89±0.17	0.1257±0.0010	0.9996
15	6.57±0.25	0.1232±0.0014	0.9991	6.52±0.17	0.1235±0.0010	0.9996

are minimal for the set Fn+An; (2) for the set Fn+An, r exhibits the nearest value to 1; (3) the including of Dn kinetic models into the set containing Fn+An kinetic models determines the increase of the standard deviations of a and b, and the decrease of r; (4) for the sets Dn^t and Dn, the standard deviations of a and b are higher than for a^* and b^*. These results are also in agreement with our theoretical considerations.

If a and b and a^* and b^* respectively, are correlated by a supercorrelation relation (Eq. (3)), one obtains the values of the invariant activation parameters listed in Table 5. One notes that all E_{inv} values are in good agreement with the E value for which the simulation was performed. As was expected, the E_{inv} and $\ln A_{\text{inv}}$ values closest to those used for simulations were obtained for the set Fn+An.

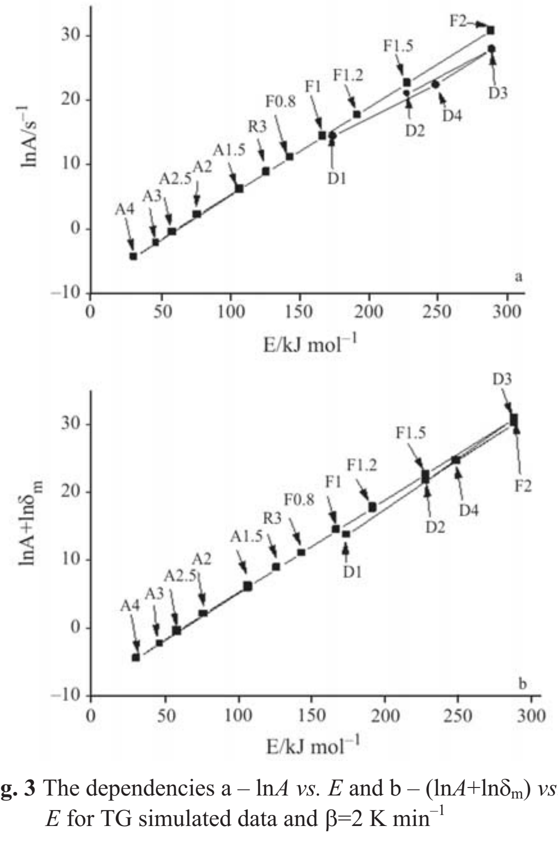

Fig. 3 The dependencies a – $\ln A$ *vs.* E and b – ($\ln A+\ln\delta_m$) *vs.* E for TG simulated data and β=2 K min^{-1}

Table 6 lists the values of the CE parameters calculated using the relationships (15) and (16). Taking into account the approximations used in the derivation of these relationships, the calculated values of a and b are in good agreement with those listed in Table 3 for the set Fn+An. The introduction of these calculated values of a and b in the supercorrelation relationship (Eq. (3)) leads to the following values of the invariant parameters: E_{inv}=172.3(±4.2) kJ mol^{-1}; $\ln A_{\text{inv}}$(s^{-1})=15.49±(0.56) with $r=-0.9994$. The small differences among these last values could be explain by the approximations used in the derivation of relations (15) and (16).

The dehydrochlorination of PVC

Powdered samples of PVC were obtained through mini-emulsion polymerization in the laboratory of ICECHIM (Bucharest, Romania). The polymer had an average molecular mass of 172.000 and a number average of 64.000. The TG and DTG curves were recorded on DuPont 1090 equipment, in static air atmosphere, using open aluminum crucibles. The TG and DTG curves obtained at the heating rates of 2, 3, 4, 5 and 10 K min^{-1} were reported in a previous paper [35]. The results reported in another previous paper [27] dedicated to the application of IKP method for the evaluation of the kinetic parameters corresponding to this kind of PVC will be used to check the theoretical results from the actual work. Like in the previous paper [27], for application of IKP method, the following conversion functions are considered: Fn

Table 5 Invariant activation parameters for the considered sets of conversion functions (TG simulated data)

Set of conversion functions	$a_\beta=\ln A_{inv}-b_\beta E_{inv}$			$\alpha_\beta^*=\ln A_{inv}+\ln\delta_m-b_\beta^* E_{inv}$		
	$\ln A_{inv}$/s^{-1}	E_{inv}/kJ mol^{-1}	$-r$	$\ln A_{inv}+\ln\delta_m$	E_{inv}/kJ mol^{-1}	$-r$
Fn+An	14.30±0.02	167.0±0.1	1	14.30±0.02	167.0±0.1	1
Dn^t	14.48±0.14	166.4±1.2	0.9999	12.87±0.08	167.6±0.6	1
Dn	13.26±0.18	164.0±1.6	0.9999	13.38±0.09	167.9±0.7	1
Fn+An+Dn^t	13.65±0.08	166.8±0.1	1	14.02±0.01	167.0±0.1	1
Fn+An+Dn	13.67±0.00	166.8±0.00	1	14.10±0.01	167.0±0.1	1

Table 6 The calculated values of *a* and *b* for TG simulated data

β/K min^{-1}	T_m/K	$\overline{\ln E}$/J mol^{-1}	$\overline{1/E}$/mol kJ^{-1}	$-a$/s^{-1}	b/mol kJ^{-1}
2	937.6	11.6±0.7	0.0115±0.0086	8.61	0.1398
5	974.2	11.6±0.7	0.0115±0.0087	7.77	0.1351
10	1003.1	11.6±0.7	0.0116±0.0088	7.14	0.1316
15	1024.6	11.6±0.7	0.0116±0.0089	6.78	0.1291

Table 7 Invariant activation parameters for the considered sets of conversion functions (PVC non-isothermal degradation)

Set of conversion functions	$a_\beta=\ln A_{inv}-b_\beta E_{inv}$			$a_\beta^*=\ln A_{inv}+\ln\delta_m-b_\beta^* E_{inv}$			*a* and *b* calculated using Eqs (15) and (16)		
	$\ln A_{inv}$/s^{-1}	E_{inv}/kJ mol^{-1}	$-r$	$\ln A_{inv}+\ln\delta_m$	E_{inv}/kJ mol^{-1}	$-r$	$\ln A_{inv}$/s^{-1}	E_{inv}/kJ mol^{-1}	$-r$
Fn+An	16.34±1.41	98.4±6.2	0.9942	16.34±1.41	98.4±6.2	0.9942	17.22±0.59	101.6±2.6	0.9990
Dn^t	23.46±6.91	114.5±35.8	0.8792	13.89±4.59	110.0±18.2	0.9613			
Dn	23.47±6.58	113.2±34.3	0.8854	14.80±3.64	106.0±15.0	0.9711			
Fn+An+Dn^t	17.21±2.50	98.8±11.4	0.9804	16.89±1.67	99.8±7.4	0.9918			
Fn+An+Dn	17.19±2.42	98.6±11.1	0.9816	16.85±1.50	99.5±6.7	0.9934			

for n=1, 1.2, 1.4, 1.6, 1.8, 2, 2.2, 2.4 and 2.6; An for n=0.5 and 1.5; Dn for n=1, 2, 3 and 4. The evaluation of the activation parameters corresponding to each conversion function and heating rate was performed by D method based on Eq. (17) and for $0.05\leq\alpha\leq0.70$ (in this range of α, E is constant ($\approx$104 kJ mol^{-1})).

In Figs 4a and b the curves $\ln A$ *vs.* E and ($\ln A+\ln\delta_m$) *vs.* E for β=4 K min^{-1} are shown. Similar curves were obtained for all heating rates. The inspection of these curves leads to observations similar with those mentioned at the analysis of the TG simulated data.

By applying the procedures used for analysis of simulated data, the values of the invariant activation parameters listed in Table 7 were obtained.

One notes that: (1) the relative errors of E_{inv} is lower than 10% only for the sets Fn+An , Fn+An+Dn^t and Fn+An+Dn (the last two sets only for the supercorrelation of a^* and b^*); (2) the maximum value of $|r|$ was obtained for the set Fn+An; (3) for the sets Dn^t and Dn, both plots a *vs.* b and a^* *vs.* b^* are not linear; (4) taking into account the standard deviations of $\overline{\ln E}$ and $\overline{(1/E)}$, and the approximations used in the derivation of these relations (15) and (16), the calculated values E_{inv} and $\ln A_{inv}$ are in a satisfactory agreement with those corresponding to Fn+An kinetic models.

Dehydration of $CaC_2O_4\cdot H_2O$

Although the IKP method can be applied only if the activation energy is independent on α, in a series of works, from which we mention [20–23], this method was used without previous evaluation of the dependence E *vs.* conversion degree. In this paper, we want to put in evidence the effect of the set of kinetic models on the values of the invariant activation parameters in the case of $CaC_2O_4\cdot H_2O$ dehydration that exhibit a strong dependence of E on α.

The TG curves corresponding to the dehydration of $CaC_2O_4\cdot H_2O$ at the heating rates 0.987, 2.353, 4.988 and 9.573 K min^{-1} were reported in [36]. In a previous paper [6], it was obtained that E evaluated by isoconversional differential method suggested by Friedman [37] decreases from 134.8 kJ mol^{-1} for α=0.1 to 66.0 kJ mol^{-1} for α=0.9.

For application of the IKP method the following conversion functions were used: Fn for n=1/2

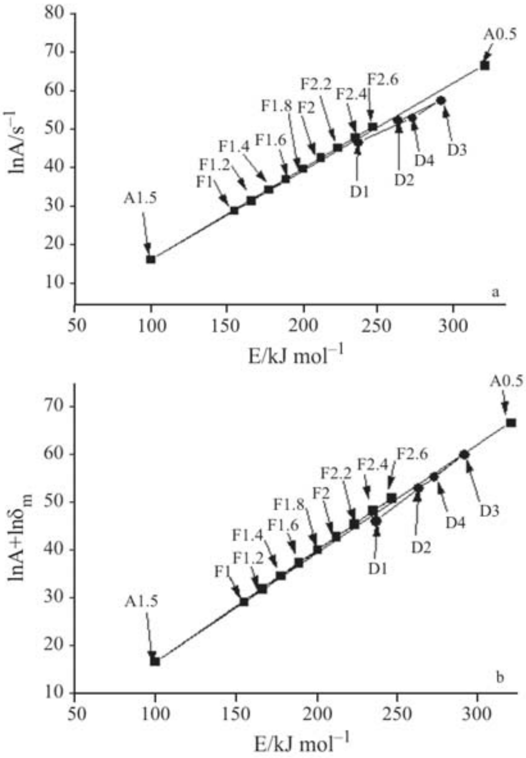

Fig. 4 The dependencies a – ln$A$ *vs.* E and b – (lnA+lnδ_m) *vs.* E for non-isothermal degradation of PVC and β=4 K min^{-1}

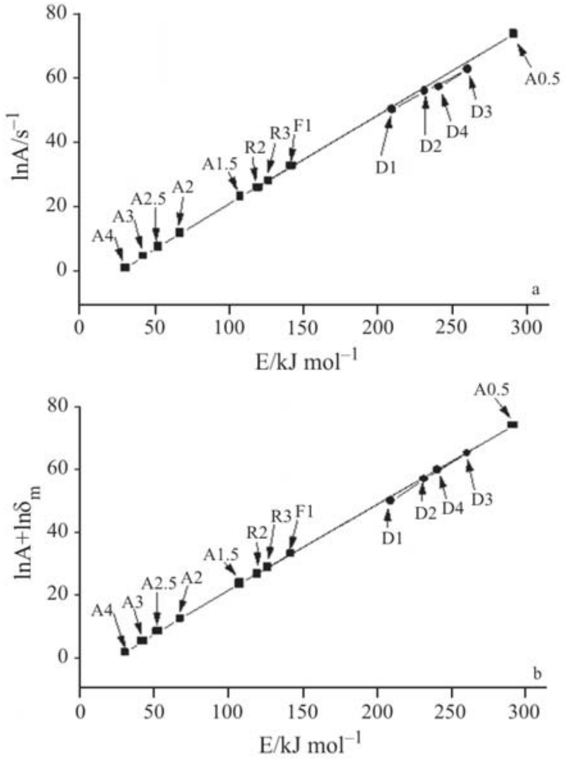

Fig. 5 The dependencies a – ln$A$ *vs.* E and b – (lnA+lnδ_m) *vs.* E for dehydration of $CaC_2O_4{\cdot}H_2O$ and β=2.353 K min^{-1}

(R2 model), 2/3 (R3 model) and 1; An for n= 0.5, 1.5, 2.0, 2.5, 3.0 and 4.0; and Dn for n=1, 2, 3 and 4. The evaluation of the activation parameters corresponding to each heating rate and conversion function was performed by the Coats–Redfern method [38] that is based on the relation:

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{\beta E}-\frac{E}{RT} \qquad (18)$$

The plots $[\ln g(\alpha)]/T^2$ *vs.* $(1/T)$ for a given analytical form of $g(\alpha)$ should be a straight line from whose parameters E and ln$A$ are evaluated. The range of α was $0.1\leq\alpha\leq0.9$.

In Figs 5a and b the curves ln$A$ *vs.* E and (ln$A$+lnδ_m) *vs.* E for β=2.353 K min^{-1} are shown. Similar curves were obtained for all heating rates. The inspection of these curves leads to observations similar with those mentioned at the analysis of the TG simulated data and TG data for the non-isothermal degradation of PVC. It turns out that the theoretical results concerning the CE are also confirmed for the dehydration of $CaC_2O_4{\cdot}H_2O$.

By applying the procedures used for analysis of simulated data and PVC dehydrochlorination data, the values of the invariant activation parameters listed in Table 8 were obtained.

One notes that: (1) the relative errors of E_{inv} are higher than 10% for the sets Dn^t and Dn and the supercorrelation of a* and b*; (2) a strong dependence of the invariant activation parameters of the set of con-

Table 8 Invariant activation parameters for the considered sets of conversion functions (dehydration of $CaC_2O_4{\cdot}H_2O$)

Set of conversion functions	$a_\beta=\ln A_{inv}-b_\beta E_{inv}$			$a_\beta{}^*=\ln A_{inv}+\ln\delta_m-b_\beta{}^*E_{inv}$			a and b calculated using Eqs (15) and (16)		
	$\ln A_{inv}$/s^{-1}	E_{inv}/kJ mol^{-1}	$-r$	$\ln A_{inv}+\ln\delta_m$	E_{inv}/kJ mol^{-1}	$-r$	$\ln A_{inv}$/s^{-1}	E_{inv}/kJ mol^{-1}	$-r$
Fn+An	24.76±1.61	114.0±5.8	0.9974	24.76±1.61	114.0±5.8	0.9974			
Dn^t	11.86±0.37	50.0±1.6	0.9990	90.46±27.45	341.6±90.2	0.9369			
Dn	10.30±0.30	44.9±1.3	0.9992	42.11±7.26	181.1±24.8	0.9817	42.46±7.64	174.7±27.0	0.9769
Fn+An+Dn^t	18.32±0.45	91.7±1.7	0.9997	22.02±0.95	104.8±3.5	0.9989			
Fn+An+Dn	18.24±0.45	91.4±1.7	0.9997	22.81±1.06	107.3±3.9	0.9987			

version functions; (3) calculated values of *a* and *b* are not correlated through supercorrelation relationship.

An interesting result appears by comparing, for each considered kinetic model, the maximum deviations of the activation energy, which is due to the change of this quantity with the heating rate ($e=E_{\max}-E_{\min}/E_{\min}\cdot 100$). For TG simulated data and PVC non-isothermal degradation that exhibit E independent on α, $0\%\leq e\leq 9.0\%$, while for dehydration of $CaC_2O_4\cdot H_2O$, for which E is strongly dependent on α, $47.9\%\leq e\leq 64.5\%$.

Conclusions

In this paper, the following problems concerning the apparent compensation effect (CE) due to the change of the conversion function and on which IKP method is based were discussed: (1) the explanation of this kind of CE; (2) the choice of the set of the conversion function for which CE is valid; (3) the dependencies of CE parameters on the heating rate and the temperature at which the reaction rate has a maximum value.

Starting with the logarithmic form of the Kissinger law, it was pointed out that CE relationship is valid only for Fn+An kinetic models, while for Dn kinetic models and a certain heating rate ($\ln A+\ln\delta_m$) *vs.* E is a straight line. Therefore, when using IKP method, one should not include the diffusion models in the calculations.

The dependencies of CE parameters on the heating rate and the temperature corresponding to the maximum reaction rate were derived.

The theoretical results were checked and discussed for the following sets of non-isothermal data: (1) TG simulated data for single first order reaction; (2) TG data for non-isothermal degradation of PVC and (3) non-isothermal dehydration of $CaC_2O_4\cdot H_2O$.

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