THE KISSINGER LAW AND ISOKINETIC EFFECT
Part II. Experimental analysis

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Abstract

On the basis of copper sulphate pentahydrate thermal dissociation, for analyzed reactions I to IV, 6 thermokinetic equations was discussed. Arrhenius law parameters were determined and the isokinetic effect (IE) and Kissinger law appearing was analyzed. It was found that only dependence resulting from isokinetic effect, in the form $k_m = q/T_m$, relates to the suitable thermokinetic Eq. (2) and Kissinger law in modified form (14). The confirmation was made that the possibility of determining the averaged activation energy from thermokinetic equations using suitable correction coefficients exists.

Introduction and aim of the work

It has been shown that the most known thermokinetic equations $g(\alpha)$ *vs. T* – for which pairs of the activation energy (E) and the pre-exponential factor (A) fulfil the iso-kinetic effect (IE) – may not be convergent with Kissinger law [1–4].

The aim of the work is experimental verification of liaisons being discussed on the base of $CuSO_4 \cdot 5H_2O$ thermal dissociation (and dehydration of $CaC_2O_4 \cdot H_2O$) with 5 heating rates.

Basic assumptions

According to equations, formulas and symbols carried in work [1] the assumption was made with following results elaborating schedule:

1) Equations in integral form:

$$g(\alpha) = \frac{ART^2}{qE} e^{-E/RT} \tag{1}$$

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$$g(\alpha) = \frac{AT}{q} e^{-E/RT} \tag{2}$$

$$g(\alpha) = 0.00484 \frac{AE}{qR} e^{-1.0516E/RT} \tag{3}$$

2) Equations (1) to (3) in integral form after introducing the Kissinger law for $\delta=1$:

$$g(\alpha) = \left(\frac{T}{T_m}\right)^2 e^{\frac{E}{RT_m}\left(1-\frac{T_m}{T}\right)} \tag{4}$$

$$g(\alpha) = \left(\frac{T}{T_m}\right) \frac{E}{RT_m} e^{\frac{E}{RT_m}\left(1-\frac{T_m}{T}\right)} \tag{5}$$

$$g(\alpha) = 0.00484 \left(\frac{E}{RT_m}\right)^2 e^{\frac{E}{RT_m}\left(1-\frac{T_m}{T}\right)} \tag{6}$$

3) As $g(\alpha)$ functions we carry in 13 models: F1, F2, F3, R1, R2, R3, A2, A3, D1 to D4, 2F1-R1,

4) For all solutions from (1) to (6) we analyze IE [5] in form:

$$\ln A = \frac{E}{RT_m} + \ln k_m , \text{ for } q=\text{idem} \tag{7}$$

5) We make selection of equations from (1) to (6) using:

$$\text{a) criterion } g(\alpha_m)=1, \text{ proposed in [1],} \tag{8}$$

$$\text{b) statistic criterion: } r^2 \geq 99\%, \tag{9}$$

thus, in result, we obtain the most substantial models from 13 analyzed;

6) We verify the reasonableness of formulas (10) to (12):

$$k_m = \frac{qE}{RT_m^2} = \frac{q}{T_m} u_m \tag{10}$$

$$k_m = \frac{q}{T_m} \tag{11}$$

$$k_m = \frac{qR}{0.005E} \tag{12}$$

taking k_m for selected models;

7) We assume control points:

a) the Kissinger law in Wendlandt's version [6]:

$$\ln\left(\frac{q}{T_\mathrm{m}^2}\right)=\ln\frac{AR}{E}-\frac{E}{RT_\mathrm{m}}, \; E=E_\mathrm{I} \tag{13}$$

b) the Kissinger law in version [1]:

$$\ln\left(\frac{q}{T_\mathrm{m}}\right)=\ln A-\frac{E}{RT_\mathrm{m}}, \; E=E_\mathrm{II} \tag{14}$$

c) averaged activation energy according to [1]:

$$\overline{\overline{E}}=E/b \tag{15}$$

where

b=1 for F and R models,
b=2 for D models,
b=1/2 for A2 model and *b*=1/3 for A3 model,

so from Eqs (1) to (6) we obtain the activation energies marked with $\overline{E}_1$ to $\overline{E}_6$ symbols, where indices 1 to 6 correspond to adequate Eqs (1) to (6).

Some remarks on Eqs (2), (5) and (11)

In previous work [1] the relation resulting from condition:

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}=0, \; T=T_\mathrm{m} \tag{16}$$

was introduced into Eq. (2) in form:

$$\frac{AT_\mathrm{m}}{q}e^{-E/RT_\mathrm{m}}=\left(\frac{E}{E+RT_\mathrm{m}}\right)^2 \tag{17}$$

and other form of equation than it is presented by Eq. (5) was obtained:

$$g(\alpha)=\frac{T}{T_\mathrm{m}}\left(\frac{E}{E+RT_\mathrm{m}}\right)^2 e^{\frac{E}{RT_\mathrm{m}}\left(1-\frac{T_\mathrm{m}}{T}\right)} \tag{18}$$

Equation (17) was presented:

$$k_\mathrm{m}=\frac{q}{T_\mathrm{m}}\left(\frac{E}{E+RT_\mathrm{m}}\right)^2 \tag{19}$$

and formula similar to Eq. (11) was obtained.
For condition:

$$E>>RT_\mathrm{m} \tag{20}$$

Equations (18) and (19) simplify themselves into relation:

$$g(\alpha) = \frac{T}{T_{\mathrm{m}}} e^{\frac{E}{RT_{\mathrm{m}}}\left(1 - \frac{T_{\mathrm{m}}}{T}\right)} \qquad (21)$$

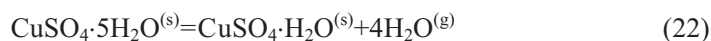and into Eq. (11), respectively.

Experimental

Thermal dissociation of copper sulphate pentahydrate (Thermal Analysis Tutorial Kit, ME-29710, Mettler TA-Test Sample) was carried out using Mettler TG-50 thermo-balance in TA-4000 thermoanalytic system in nitrogen (200 mL min^{-1}). Figure 1 presents
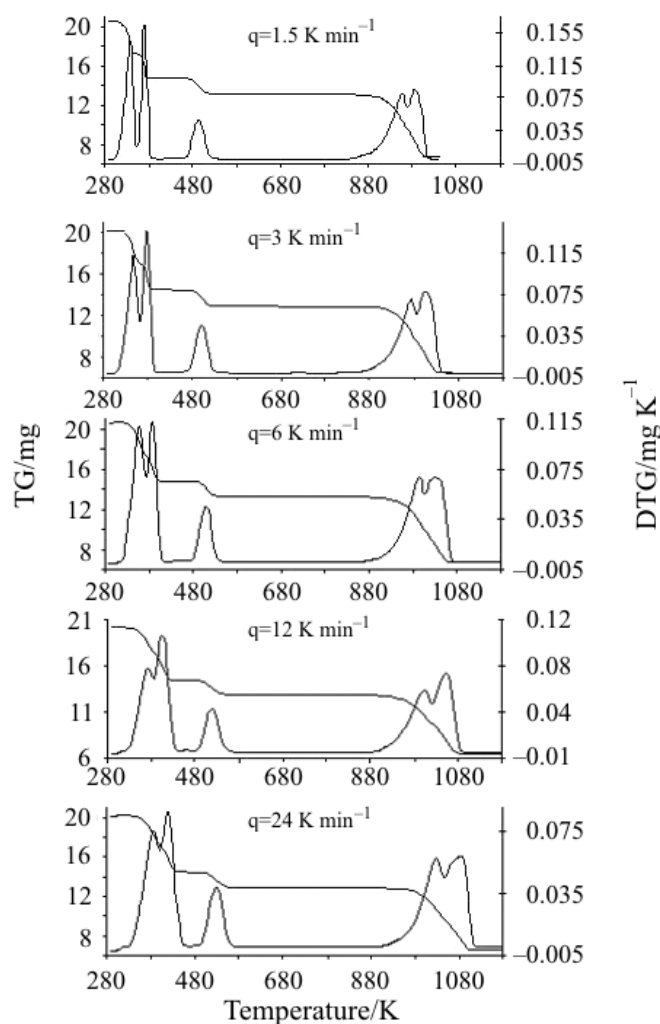
Fig. 1 TG and DTG curves of CuSO$_4$·5H$_2$O thermal dissociation for five heating rates (q)

adequately registered (and smoothed) TG and DTG curves. Calcium oxalate monohydrate (purity: 99.999%, Aldrich) was dehydrated in Mettler Toledo TGA/SDTA-851^e/STAR^e thermobalance in dynamic atmosphere of air (100 mL min^{-1}). Mass samples (20±0.01 mg), platinum open crucible and 5 heating rates: q=1.5, 3, 6, 12 and 24 K min^{-1} were analogous for both substances.

The choice of $CuSO_4 \cdot 5H_2O$ results from the fact that its thermal dissociation is well described in literature. The dissociation curves of this model substance are published in atlases of thermogravimetric curves [7]. They reflect simple reactions:

$$CuSO_4 \cdot 5H_2O^{(s)} = CuSO_4 \cdot H_2O^{(s)} + 4H_2O^{(g)} \tag{22}$$

$$CuSO_4 \cdot H_2O^{(s)} = CuSO_4^{(s)} + H_2O^{(g)} \tag{23}$$

$$CuSO_4^{(s)} = CuO^{(s)} + SO_3^{(g)} \tag{24}$$

From Fig. 1 and [8–13] comes that the course of reactions (22) to (24) is more complicated and it is presented in Table 1 in chronological conception.

For further considerations the following reactions were taken into account:

reaction I   Table 1
reaction II   Table 1
reaction III   Table 1 and (23)
reaction IV   (24) although from Fig. 1 and Table 1 and [8, 10, 12, 13] comes
that this reaction courses in two stages.

Results

The correlations analysed formed a large amount of graphic illustrations (1676). Figure 2 shows the course of performed calculations. Because of large number of dependencies only selected ones will be presented. Apart from basic relationships ($g(\alpha)$ *vs. T* according to Eqs (1) to (6)) the criterion (8) is illustrated by Fig. 3 (reaction III). For reactions I to IV models A2, A3 the and F1 were selected, what is maybe reflecting, but according to work [1] we can expect that condition (8) is fulfilled only by some models. Figure 4 presents analysis of IE (7) for reaction I (Fig. 4a – 13 models) and after selection (Fig. 4b – 3 models). Since there are invisible control points resulting from Eqs (13), (14) and formula (15) on Fig. 4, therefore, analysis of IE (7) in the three-model version is given in Fig. 5.

If we say that in spite of differences common IE (7) exists for any heating rate (q), then control points E_I, $\overline{E}_1$, $\overline{E}_3$ to $\overline{E}_6$ also form IE, however E_{II} and $\overline{E}_2$ are connected with lower ln$A$ value (Fig. 5a) (reaction IV, Eq. (4)). On the contrary, when control points E_{II} and $\overline{E}_2$ are placed on the IE straight line (7), then remaining ones deviate from IE insignificantly, but ln$A$ value is slightly higher (Fig. 5b) (reaction I, Eq. (2)).

One can say that the case illustrated on Fig. 5a is remarked in [14] (activation energy is connected with lower ln$A$ value). It was also concluded that for reactions I and II activation energies according to (13) and (14) are significantly lower than values resulted from Eqs (1) to (6) and averaged by calculation (15). With mentioning

Table 1 Reactions of $CuSO_4 \cdot 5H_2O$ thermal dissociation

Reaction number	Reactions	References	Remarks (E/kJ mol^{-1})
I	Ia: $CuSO_4 \cdot 5H_2O^{(s)} \rightarrow CuSO_4 \cdot 3H_2O^{(s)} + 2H_2O^{(l)}$ Ib: $2H_2O^{(l)} \rightarrow 2H_2O^{(g)}$ (from satd. soln.)	[4, 6, 7]	$t = 85°C^a$ [4], $E=188.4$ [7]
II	$CuSO_4 \cdot 3H_2O^{(s)} \rightarrow CuSO_4 \cdot H_2O^{(s)} + 2H_2O^{(g)}$	[4–7]	$t = 115°C^a$ [4], $E=199.7$ [7] $t = 40–50°C^b$ [5], $E=65.3$ [5]
III	$CuSO_4 \cdot H_2O^{(s)} \rightarrow CuSO_4^{(s)} + H_2O^{(g)}$	[4, 7]	$t = 230°C$ [4], –
IV	IVa: $CuSO_4^{(s)} \rightarrow CuSO_4 \cdot CuO^{(s)} \rightarrow CuO^{(s)} + SO_3^{(g)}$ IVb: $2CuSO_4^{(s)} \rightarrow CuO \cdot CuSO_4^{(s)} + SO_3^{(g)}$ IVc: $CuO \cdot CuSO_4^{(s)} \rightarrow 2CuO^{(s)} + SO_3^{(g)}$ IVd: $SO_3^{(g)} \rightarrow SO_2^{(g)} + 1/2O_2^{(g)}$	[6, 8, 9]	$t \geq 750°C$ ($CuSO_4 \cdot CuO$) [6, 9] $E = 238.6 \pm 29.3$ [9] $E = 280.5 \pm 33.5$ [9]

a maximum from DTA curve
b low pressure (in vacuo), ln$A$=12.18 (A in min^{-1})

Table 2 Parameters of both Arrhenius law resulting from Eqs (1) to (6) and Kissinger law in version (13) and (14)

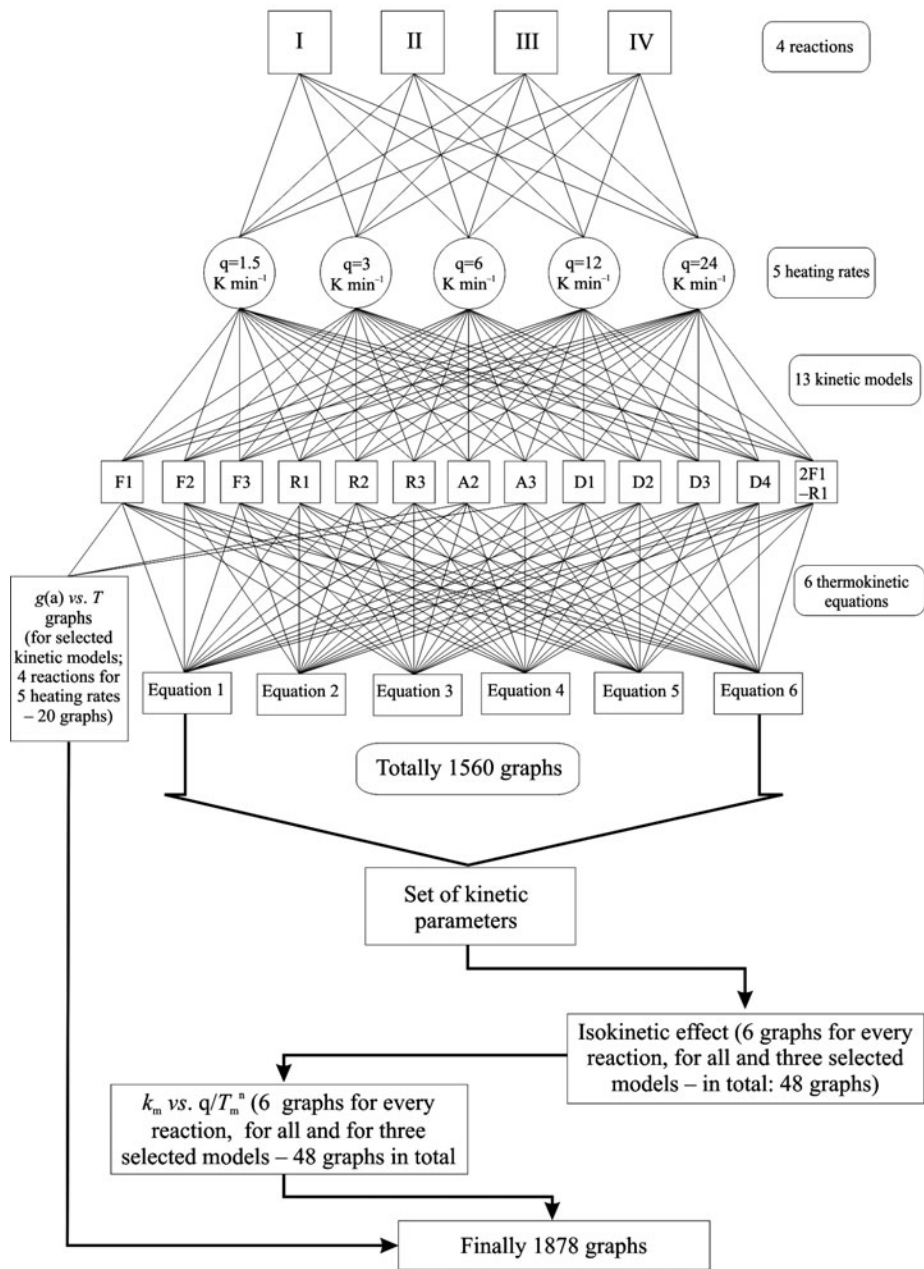| Reaction number		I		II		III		IV	
Kinetic parameters		E^a, $\overline{E}^b$/ kJ mol^{-1}	$\ln A^a$, $\ln \overline{A}^b$/ min^{-1}	E^a, $\overline{E}^b$/ kJ mol^{-1}	$\ln A^a$, $\ln \overline{A}^b$/ min^{-1}	E^a, $\overline{E}^b$/ kJ mol^{-1}	$\ln A^a$, $\ln \overline{A}^b$/ min^{-1}	E^a, $\overline{E}^b$/ kJ mol^{-1}	$\ln A^a$, $\ln \overline{A}^b$/ min^{-1}
Eq. (11)		56.4	17.7	62.8	18.1	164.0	37.9	233.8	25.5
Eq. (12)		59.4	15.8	66.1	16.1	168.2	35.3	248.3	23.8
Eq. (1)	all models	104.6	35.7	180.2	55.0	190.2	44.5	244.1	26.0
	three models	102.2	30.2	172.1	50.4	168.1	38.1	238.7	25.2
Eq. (2)	all models	108.2	33.5	185.6	52.0	195.8	41.0	255.0	24.6
	three models	105.3	29.8	172.2	50.7	174.1	37.8	240.2	24.1
Eq. (3)	all models	107.2	37.0	182.4	56.2	191.4	45.1	250.4	26.9
	three models	105.0	32.1	174.4	53.2	170.0	37.2	246.7	22.1
Eq. (4)	all models	108.3	37.5	185.6	57.5	197.1	45.0	260.4	27.7
	three models	102.8	32.2	178.0	52.1	174.8	40.2	250.7	24.2
Eq. (5)	all models	106.4	36.5	182.4	58.5	191.6	45.2	240.1	26.5
	three models	101.1	30.1	170.7	55.7	183.2	38.7	233.1	26.2
Eq. (6)	all models	109.5	37.9	186.3	59.1	198.8	46.2	256.4	28.0
	three models	107.2	32.8	175.1	56.7	179.6	38.5	242.7	24.1

[a]for Eqs (11) and (12)
[b]for Eqs (1) to (6)

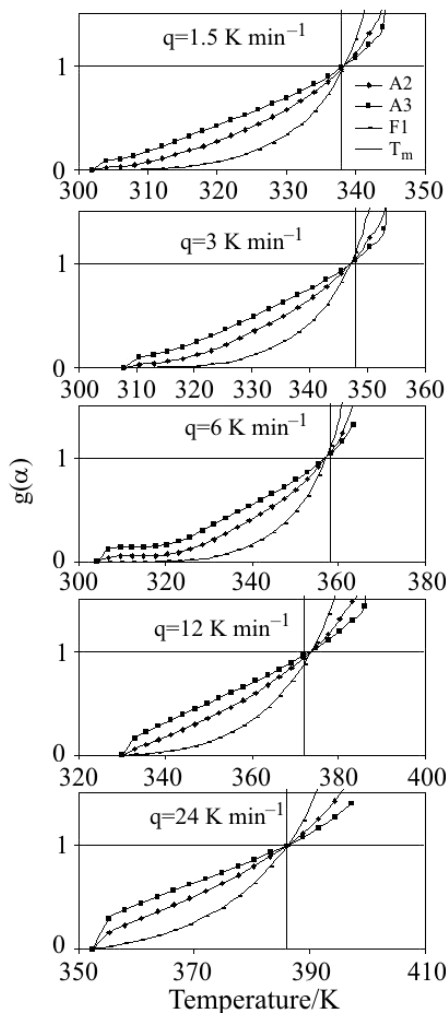**Fig. 2** Review of calculating procedures for reactions I to IV

**Fig. 3** Graphical analysis of $g(\alpha_m)=1$, criterion for reaction III

that for every case activation energies according to (13) and (14) are similar, so we can say that the Kissinger law modification leads to similar values. Table 2 shows the comparison of estimated kinetic parameters. The table recapitulates results of calculations showed as an example on Figs 4 and 5, and demonstrates that it is necessary to verify reasonableness of formulas (10) to (12).

Figure 6 shows k_m (Eq. (7)) dependence linearly connected with heating rate (q) for corresponding formulas – version on Fig. 6a is related to all 13 models and Fig. 6b for 3 chosen models (A2, A3, F1) only. From the fact that in many cases we obtain linear relationships (straight line with one parameter), that's why the comparison of
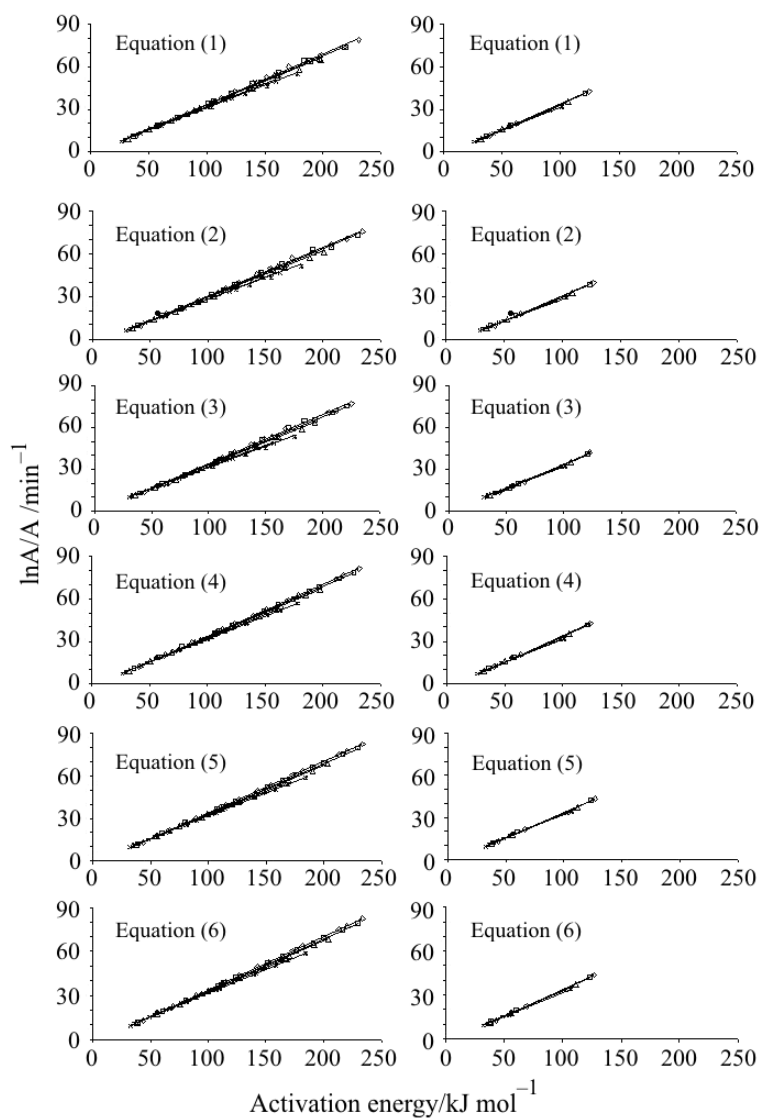
Fig. 4 The IE analysis for reaction I for: a – 13 $g(\alpha)$ models, b – A2, A3 and F1 models; q=idem and the next, q=var.

determined activation energies with values presented in Table 2 is only possible verification. Table 3 shows that we did not gain conformity of determined values with formule (10) and (12) thus, we experimentally proved that only Eq. (2), the isokinetic effect (7) and modified Kissinger law (14) are congruent.
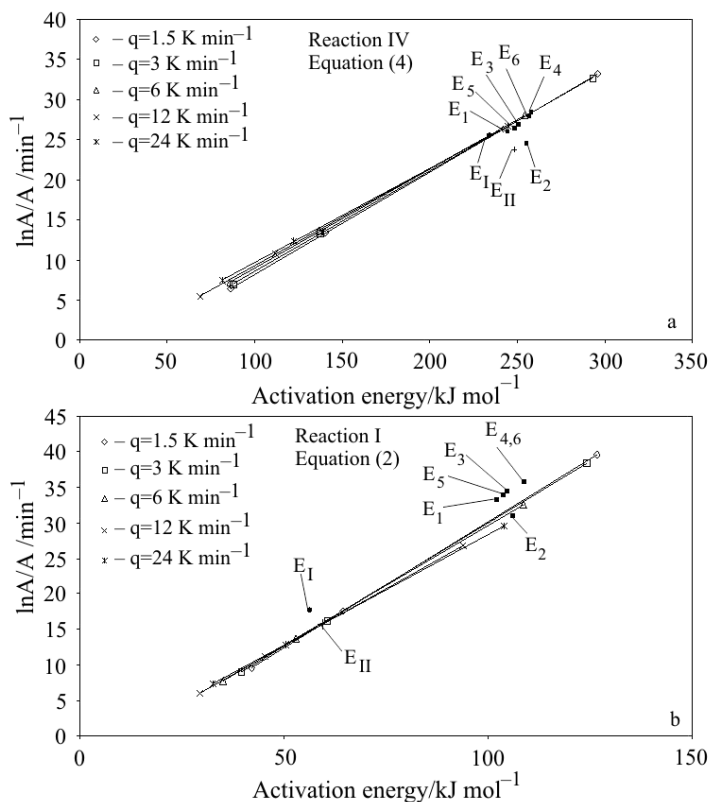
Fig. 5 The IE analysis for reactions: a – IV, b – I. A2, A3 and F1 models with control
points according to Eqs (13), (14) and formula (15); q=idem and the next, q=var.

It is necessary to say that formula (11) has to be fulfilled for trend coefficient
equal 1 and for one-parametric straight line determination coefficient $\rho^2=1$ (Fig. 6b,
symbol (2, 11)).

Discussion

The other question is taking an attitude with regard to determination possibility of the
Arrhenius law coefficients (activation energy (E) and pre-exponential factor (A)) in
the case studied, using calculating procedures applied in the work. For this purpose
Table 1 was filled up using data from Table 4. There is standard enthalpy of reac-
tions I to IV (T=298 K) given in the Table which was calculated from the formula:

$$\Delta H_{298} = \sum \nu_i \Delta H_{f,i} \tag{25}$$

taking individual enthalpies of formation $\Delta H_{f,i}$ from Barin's tables [15].
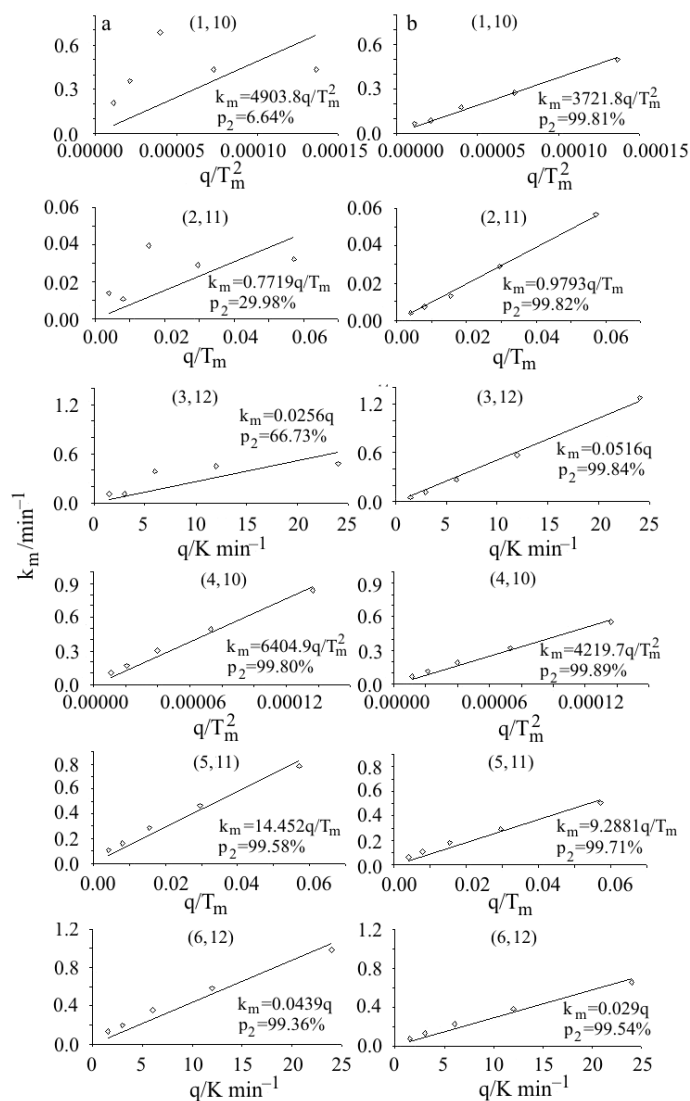
Fig. 6 Analysis of formulas (10) to (12) resulting from IE (7) for: a – 13 $g(\alpha)$ models,
b – A2, A3 and F1 models. Reaction II. The symbol on figure, for example
(1, 10), means formula (10) analysis by the $g(\alpha)$ function No. (1)

Tables 1 and 4 show that all Eqs (1) to (6) lead to congruent values of activation energy after averaging by formula (15). However we can note wider and wider divergence of these values for reactions III and IV. Good accordance with [9] was gained for reaction IV, but for reactions I and II it is lower, in relation to [11]. As we said before, the other question is that for reactions I and II the Kissinger laws (13) and (14) determine much lower activation energies, even below standard enthalpy of reaction

Table 3a The analysis of formulas (10) to (12) for reactions I to IV (Fig. 6 presents the part of analysis)

Reaction number		I	II	III	IV
Activation energy calculated from formula (10) using:					
Eq. (1)	all models	4928.20	4903.8	5995.6	8135.7
		41.00	40.8	49.8	67.6
		98.08	6.64	98.56	88.4
	three models	2314.10	3721.8	4229.8	5539.5
	Slope in formula (10)	19.20	30.9	35.2	46.1
	E/kJ mol^{-1}	99.15	99.81	99.76	99.94
	ρ^2/%				
Eq. (4)	all models	3807.60	6404.9	7641.4	8966.7
		31.70	53.3	63.5	74.5
		99.07	99.8	99.85	99.89
	three models	2661.80	4219.7	4313.3	6287.1
		22.10	35.1	35.9	52.3
		99.67	99.89	97.17	99.81
Activation energy calculated from formula (12) using:					
Eq. (3)	all models	0.0838	0.0256	0.0231	0.0248
		20.70	67.7	75.0	69.8
		95.61	66.73	97.0	90.32
	three models	0.0838	0.0516	0.0479	0.0347
	Slope in formula (12)	20.7	33.6	36.2	49.9
	E/kJ mol^{-1}	95.61	99.84	99.93	99.92
	ρ^2/%				
Eq. (6)	all models	0.0262	0.0439	0.0278	0.0078
		66.1	39.5	62.3	222.1
		99.36	99.36	99.84	99.90
	three models	0.0183	0.0290	0.0164	0.0055
		94.7	59.7	105.6	314.9
		99.8	99.54	99.45	99.54

Table 3b The analysis of formula (11) for reaction I to IV

| Reaction number			I	II	III	IV
	all models	Slope	1.4482	0.7719	0.7793	1.0540
		ρ^2/%	96.90	29.98	98.61	96.48
Eq. (2)						
	three models	Slope[a]	**0.9991**	**0.9793**	**1.0318**	**1.0191**
		ρ^2/%	**100**	**99.82**	**99.90**	**100**
Slopes in formula (11) for:						
	all models	Slope	9.0571	14.4520	12.84	7.8332
		ρ^2/%	99.01	99.58	96.59	99.45
Eq. (5)						
	three models	Slope[b]	6.1174	9.2881	7.2122	5.6371
		ρ^2/%	99.63	99.71	94.73	99.60

[a] slope=1
[b] slope>1

of dissociation (ΔH_{298}). We can explain it by the fact of large influence of reaction of dehydration course in low temperatures (Fig. 1), where it is necessary to take enthalpy of water evaporation into account, it means:

$$H_2O^{(l)} \rightarrow H_2O^{(g)}, \Delta H_{298} = 44.0 \text{ kJ mol}^{-1} \quad (26)$$

According to Table 4, for reactions I to III enthalpy of water molecule detaching in liquid state is very small, about 24–29 kJ mol^{-1}. For that reason for reactions I and II the Kissinger law fulfil IE (7) according to relation: lower E imply lower logarithm of pre-exponential factor ln$A$ with this difference, which results from insignificant differences of activation energies E_I (13) and E_{II} (14) – see comments to Fig. 5.

Table 4 The comparison of determined activation energies – the supplement of Table 1

Reaction number	ΔH_{298}/kJ mol^{-1}	E/kJ mol^{-1}	
		$E_I – E_{II}$	$\overline{E}_1 – \overline{E}_6$
I	111.8	56–59	101–107
Ia	111.8–2·44.0=23.8		
Ib (for 1 mole of H$_2$O)	44.0		
II	114.9 (114.9–2·44.0=26.9)	63–66	171–178
III	72.6 (72.6–44.0=28.6)	164–168	168–183
IVa	219.5	234–248	233–247
IVb	209.0 [8]/202.4[a]		
IVc	205.0 [8]/198.1[a]		
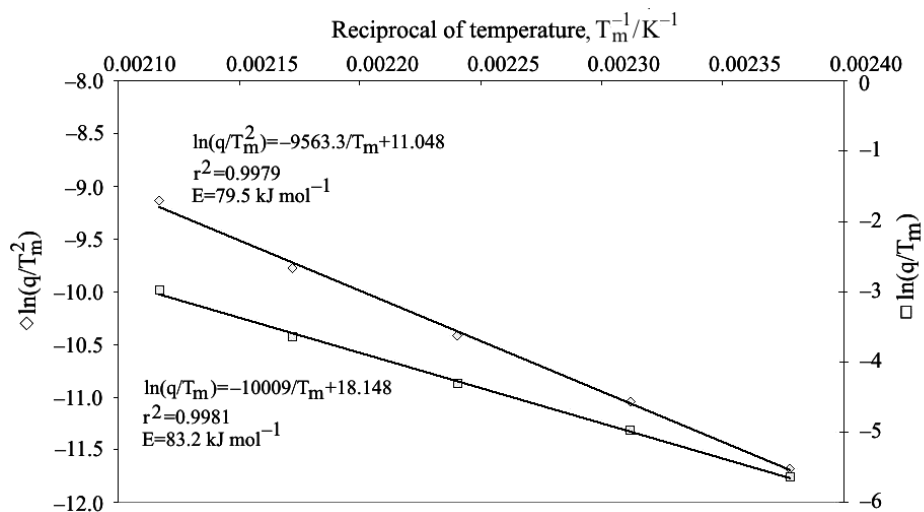
Fig. 7 The Kissinger law in versions (13) and (14) for dehydration of calcium oxalate monohydrate

Within the figure:

$\ln(q/T_m^2) = -9563.3/T_m + 11.048$
$r^2 = 0.9979$
$E = 79.5$ kJ mol^{-1}

$\ln(q/T_m) = -10009/T_m + 18.148$
$r^2 = 0.9981$
$E = 83.2$ kJ mol^{-1}

[a]ΔH_d from experimental data (Tables 1 and 2 in [8]), van't Hoff's equation

In lower pressure (in vacuo) conditions, likewise in [9], as well activation energy $E=65.3$ kJ mol^{-1}, as logarithm of pre-exponential factor ln$A=12.18$ (A in min^{-1}) fulfil IE (7) presented on Fig. 5 and real values are congruent with data in Table 4 for the Kissinger law and reaction II. Thus, the laws (13) and (14) omit energetic effects connected with physical phenomena. If we take into consideration the existence of the liquid product (H_2O) in low temperatures, the kinetic barrier (E) will be higher than the thermodynamic one (ΔH) again.

Conclusions

- Only Eq. (2), of which $g(\alpha)$ contains temperature in the first power (in AT/q expression), is congruent with isokinetic effect (7) and modified Kissinger law (14). This law is in close numerical connection with classical Kissinger law (13) (Fig. 7).
- We proved that simple dependence given by Eq. (11) provides new possibilities of analysis of thermokinetic equations and some laws connected with them. The isokinetic effect (7) contains constants k_m and T_m only when heating rate q=idem. We also confirmed that for changeable heating rates q=var, we obtain insignificantly differing numerical constants of Arrhenius equation (E and A) using Eqs (1) to (6), what is in some contradiction with the Kissinger law. Developing the left hand side of the formula (11) leads to modified Kissinger law, which averages considered constants – activation energy and pre-exponential factor (E and A).
- The studies confirm results of the works [1, 16, 17] that the possibility of activation energy determination exists using adequate averaging coefficients given by formula (15). For reactions running in lower temperatures the divergence is much lower, than for reactions of dissociation in higher temperatures. The divergence is the lower the more restrictions in kind of (9) or (8) are used.
- Assuming that for Eqs (1) to (6) one group make Eqs (1), (4) and approximations (3) and (6), and second one – (2) and (5), and that changeable heating rates form common isokinetic effect (7), the regularity was confirmed as follows:
  a) concrete activation energies E_I, $\overline{E}_1$, $\overline{E}_3$ to $\overline{E}_6$ also form the isokinetic effect and E_{II} and $\overline{E}_2$ are placed below the IE straight line,
  b) in other way, when E_{II} and $\overline{E}_2$ form IE too, then remaining ones may be placed over the IE straight line.
  It means we have to do with: *a*) a lower ln$A$ factor or *b*) a higher one.
- We confirmed that, using the Kissinger law, in some cases, we may obtain much lower activation energies and lower ln$A$ factors convergent with the isokinetic effect. The fact was confirmed for reactions I and II, where we observe two H_2O molecules detaching in low temperature range: 40–130ºC (stage I) and 90–160ºC (stage II). Basing on the results of the work, this fact may be explained by energetic effects connected with a high water evaporation enthalpy and so, with high enthalpy of reaction, in which water appears in gaseous state (thermodynamic barrier). Thus,

Kissinger law determines energetic effect connected only with the chemical reaction kinetic barrier in low activation energy (E) and pre-exponential factor (A) form.

• Taking the sequence given in conclusion first paragraph Eqs (1) to (6) may be completed with another possibility, namely Eq. (21), which differs from Eq. (5) only by omitting the expression E/RT_m. Considerations of this work and the previous one [1] point at some kind of peculiarity of Eqs (2) and (21) in relation to remaining ones. Simultaneously, they are congruent in conception of (7) and (11). In this situation what thermokinetic equations are used is conventional question. But there are more premises to take Eq. (2).

Symbols

A pre-exponential factor in Arrhenius equation/min^{-1}
α conversion degree, $0 \leq \alpha \leq 1$
b the coefficient for converting activation energy, according to (15)
$\delta = \quad -\dfrac{\mathrm{d}f(\alpha_m)}{\mathrm{d}\alpha_m}$ [1]

E activation energy/J mol^{-1}
$\overline{\overline{E}}$ averaged value of activation energy/J mol^{-1}
$f(\alpha)$ symbol of mechanism of reaction/process
$g(\alpha)$ mass integral, $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha / f(\alpha)$

ΔH enthalpy/J mol^{-1}
ΔH_{298} standard enthalpy/J mol^{-1}
IE   isokinetic effect
k rate constant/min^{-1}
n exponent, $n = 0$, 1 or 2 (Fig. 2)
q heating rate/K min^{-1}
r^2, ρ^2 determ. coefficient for the double and single parameter linear plot, respectively/%
$R =$ 8.314 J mol^{-1} K^{-1}
t, T temperature/°C or K
u dimensionless activation energy (for example $u_m = E/RT_m$)

Subscripts

I, II   according to Eqs (13) and (14), respectively
1 to 6 according to Eqs (1) to (6)
d   decomposition
i   number of chemical compound
f   formation
m   maximal reaction rate

Superscripts

(s)   solid
(l)   liquid
(g)   gaseous

References

1 A. Mianowski, J. Therm. Anal. Cal., 74 (2003) 953.

2 J. Dweck, R. S. Aderne and D. J. Sanefield, J. Therm. Anal. Cal., 64 (2001) 1163.

3 J.-J. Zhang, R.-F. Wang, J.-B. Li, H.-M. Liu and H.-F. Yang, J. Therm. Anal. Cal., 62 (2000) 747.

4 P. Păcurariu, D. Liță, R. I. Lazău, G. Kovacs and I. Lazău, J. Therm. Anal. Cal., 72 (2003) 823.

5 T. Vlase, G. Vlase, M. Doca and N. Doca, J. Therm. Anal. Cal.,72 (2003) 597.

6 D. Shultze, Differentialthermoanalyse (2. berichte Auflage), pp. 92–93, VEB Deutscher Verlag der Wissenschaften, Berlin 1971.

7 Atlas of Thermoanalytical Curves, Vol.1, p. 24, Ed. G. Liptay, Akadémiai Kiado, Budapest 1971.

8 W. W. Wentlandt, Anal. Chimica Acta, 27 (1962) 309.

9 M. M. Cooper, J. Colvin and J. Hume, Trans. Faraday Soc., 29 (1933) 576.

10 H. J. Borchardt and F. Daniels, J. Phys. Chem., 61 (1957) 917.

11 T. Ishii, T. Furumai and G. Takeya, Kogyo Kagaku Zashii, 70 (1967) 1652 (in Japan).

12 T. R. Ingraham, Trans. Metall. Soc. AIME, 233 (1965) 359.

13 T. R. Ingraham and P. Marier, ibid, p. 363.

14 A. Mianowski and T. Radko, Thermochim. Acta, 204 (1992) 281 (Fig. 1).

15 I. Barin, Thermochemical Data of Pure Substances, Vol. I: pp. 483, 492–494, 649–650, Vol. II: p.1282, VCH Verlagsgesellschaft, Weiheim 1989.

16 A. Mianowski, J. Therm. Anal. Cal., 59 (2000) 747.

17 A. Mianowski, ibid, 60 (2000) 79.