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INFLUENCE OF HEATING RATE ON KINETIC QUANTITIES OF SOLID PHASE THERMAL DECOMPOSITION

R. Bigda[1*] *and A. Mianowski*[2]

[1]Institute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland
[2]Department of Inorganic Chemistry and Technology, Silesian University of Technology, Krzywoustego 6, 44-100 Gliwice, Poland

Thermogravimetric analyses of thermal decomposition (pyrolysis, thermal dissociation and combustion) of 9 different samples were carried out in dynamic conditions at different heating rates. The kinetic parameters (E, A and k_m) of thermal decomposition were determined and interrelations between the parameters and heating rate q were analyzed. There were also relations between Arrhenius and Eyring equations analyzed for thermal decomposition of solid phase. It was concluded that Eyring theory is an element, which interconnects used thermokinetic equations containing Arrhenius law and suggests considering kinetic quantities in way relative to 3 kinetic constants (E, A and k_m). Analysis of quantities other than k_m (i.e. E, A, Δ^+H, Δ^+S) in relation to heating rate is an incomplete method and does not lead to unambiguous conclusions. It was ascertained that in ideal case, assuming constant values of kinetic parameters (E and A) towards heating rate and satisfying both Kissinger equations, reaction rate constant k_m should take on values intermediate between constants $(k_m)_1$ and $(k_m)_2$ determined from these equations. Whereas behavior of parameters E and A towards q were not subjected to any rule, then plotting relation k_m *vs.* q in the background of $(k_m)_1$ and $(k_m)_2$ made possible classification of differences between thermal decomposition processes taking place in oxidizing and oxygen-free atmosphere.

Keywords: *Arrhenius law, Eyring theory, heating rate, isokinetic effect, thermogravimetry, thermokinetic analysis*

Introduction

Heating rate, most frequently realized as $dT/d\tau=q>0$, particularly in the newest works [1–10], may influence kinetic parameters included in thermokinetic equations. In general, one looks for Arrhenius equation constants, i.e. activation energy (E) and pre-exponential factor (A):

$$k=A\mathrm{e}^{-E/RT} \tag{1}$$

or alternatively one uses temperature of maximal reaction rate (T_m):

$$k_m=A\mathrm{e}^{-E/RT_m} \tag{2}$$

On rare occasions one uses Eyring equation in form [11–14] (assuming all activity coefficients equal to 1):

$$k=\frac{k_B}{h}T\mathrm{e}^{-\Delta^+G/RT} \tag{3}$$

or in expanded form:

$$k=BT\mathrm{e}^{\Delta^+S/R}\mathrm{e}^{-\Delta^+H/RT}$$
$$B=k_B/h=0.20836\cdot10^{11}\,\mathrm{K}^{-1}\mathrm{s}^{-1} \tag{4}$$

Searched coefficients in Eq. (4) are enthalpy (Δ^+H) and entropy (Δ^+S) of activation related to the free energy of activation (Δ^+G) in form of classical formula [11]:

$$\Delta^+G=\Delta^+H-T\Delta^+S,\quad \infty>\Delta^+S>-\infty \tag{5}$$

It is necessary to stress that while typical Arrhenius equation is related in close way to reaction kinetics (though in limited temperature range), Eyring Eqs (3) and (4) are thermodynamic possibilities of interpretation of absolute reaction rate constant connected with formation of activated complex. One may also notice that form Eq. (4) is mathematically similar to other forms of Arrhenius equation, having totally different interpretation.

Internal correlation between coefficients of law Eq. (1), called compensation or isokinetic effect (IE), expressed as:

$$\ln A=\frac{E}{RT_{iso}}+\ln k_{iso},\ q=\mathrm{idem} \tag{6}$$

is also translated by Eyring Eq. (4). It comes from the fact of activation energy assigning to enthalpy part and pre-exponential factor to entropy one. There is a designation following from the fact, namely enthalpy-entropy correlation [15]. Another quantity connected with discussed issue is reaction rate constant in temperature T_m, according to Eq. (2). In Eq. (6) for dynamic conditions [16–19]:

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[*] Author for correspondence: bigda@ichpw.zabrze.pl

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Springer, Dordrecht, The Netherlands

$$T_{\text{iso}} = T_{\text{m}}, \qquad g(\alpha)=\text{var} \tag{7}$$

Comparing derivatives $d\ln k/\mathrm{d}T$ for Eqs (1) and (4) we obtain:

$$E = \Delta^{+}H + RT \tag{8}$$

and from comparison of Eq. (1) with Eq. (4), taking Eqs (8) and (5) into consideration:

$$\ln A = 1 + \ln BT + \frac{\Delta^{+} S}{R} \tag{9}$$

Because in general one determines adequate thermodynamic functions of activation from coefficients of Eqs (1), (9) may be expressed as:

$$\Delta^{+} S = R\left(\ln\frac{A}{T} - \ln B - 1 \right) \tag{10}$$

when A in s^{-1}, then $\ln B = 23.76$.

It was proved in works [12, 14, 19] that in Eqs (3)–(5) and (8)–(10) one may use T_{m} as temperature of activation.

The aim of the work

The aim of the work is searching for dependencies between E, A, T_{m} $\Delta^{+}H$, $\Delta^{+}S$ and heating rate q, taking internal correlations between kinetic quantities into consideration. Constant k_{m} may be recognized as privileged quantity with regard of its meaning connected with formation of activated complex according to Eyring theory Eq. (4). We may assume that using Eyring theory presented in works [11–14] for thermal decomposition processes makes possible carrying out similar considerations also for combustion. The more, one may use mentioned theory for reaction systems, in which it is hard to imagine existence of activated complex (tetraline+coal→naphthalene+H-coal [20, 21]).

We would like to emphasize differences between thermal decomposition processes of solids in inert and oxidizing atmosphere. The inert atmosphere processes are understood by two types of reactions, defined by the use of stoichiometric equations within following categories:

- strictly chemical and thermodynamic – thermal dissociation (usually applied to inorganic compounds and salts of organic acids),
- conventional and symbolic – pyrolysis (usually applied to chemically complicated substances – e.g. coal, polymers – or mixtures).

We are proving in present article that there are differences in behavior of kinetic rate constant (k_{m}) towards heating rate (q) between reactions taking place in different atmospheres (inert and oxidizing).

Assumptions for analytical part

- E and A are constant for q=var, what is expressed by Kissinger law in Wendtland's version [22]:

$$\ln\frac{q}{T_{\text{m}}^{2}} = \ln\frac{AR}{E} - \frac{E}{RT_{\text{m}}}, \quad E = E_{\text{I}}, A = A_{\text{I}} \tag{11}$$

and from comparison of formula (11) with Arrhenius law (2) it comes:

$$(k_{\text{m}})_{1} = \frac{qE_{1}}{RT_{\text{m}}^{2}} = A_{\text{I}}\mathrm{e}^{-E_{\text{I}}/RT_{\text{m}}} \tag{12}$$

as well as Kissinger law in form [16, 17]:

$$\ln\frac{q}{T_{\text{m}}} = \ln A - \frac{E}{RT_{\text{m}}}, \quad E = E_{\text{II}}, A = A_{\text{II}} \tag{13}$$

from which:

$$(k_{\text{m}})_{2} = \frac{q}{T_{\text{m}}} = A_{\text{II}}\mathrm{e}^{-E_{\text{II}}/RT_{\text{m}}} \tag{14}$$

Thus, there is following relation between both reaction rate constants (12) and (14):

$$(k_{\text{m}})_{1} = (k_{\text{m}})_{2}\frac{E_{1}}{RT_{\text{m}}}, \quad (k_{\text{m}})_{1} > (k_{\text{m}})_{2} \text{ because } \frac{E_{1}}{RT_{\text{m}}} >> 1 \tag{15}$$

where values of k_{m} are calculated from Eq. (2) or (4) (substituting T=T_{m}), of which parameters are interrelated by relationships (8) and (9), what leads to obtaining the same values of rate constant. T_{m} increases together with q.

- From literature data [12] follows that experimental values of E and A decrease linearly with increase of heating rate q (Fig. 1a) or strong deviations from this relationship appears at low heating rates, below q=10 K min^{-1} (Figs 1b–d).
- Free energy of activation ($\Delta^{+}G$) is approximately constant regardless of assumed functions $g(\alpha)$ [14] as well as heating rate [12, 14] (compare with Appendix A).
- Values of thermodynamic functions of activation $\Delta^{+}H$ and $\Delta^{+}S$ decrease together with heating rate increase [12].

Analysis of thermokinetic equations

Similarly to works [16, 17], two most popular thermokinetic equations in integral forms ($\mathrm{g}(\alpha)\sim T^{2}$ and $\mathrm{g}(\alpha)\sim T$ Table 1, No. 1 and 4) have been taken in order to search for relationships of reaction rate constants from condition $g(\alpha_{\text{m}}) = 1$, introducing equa-

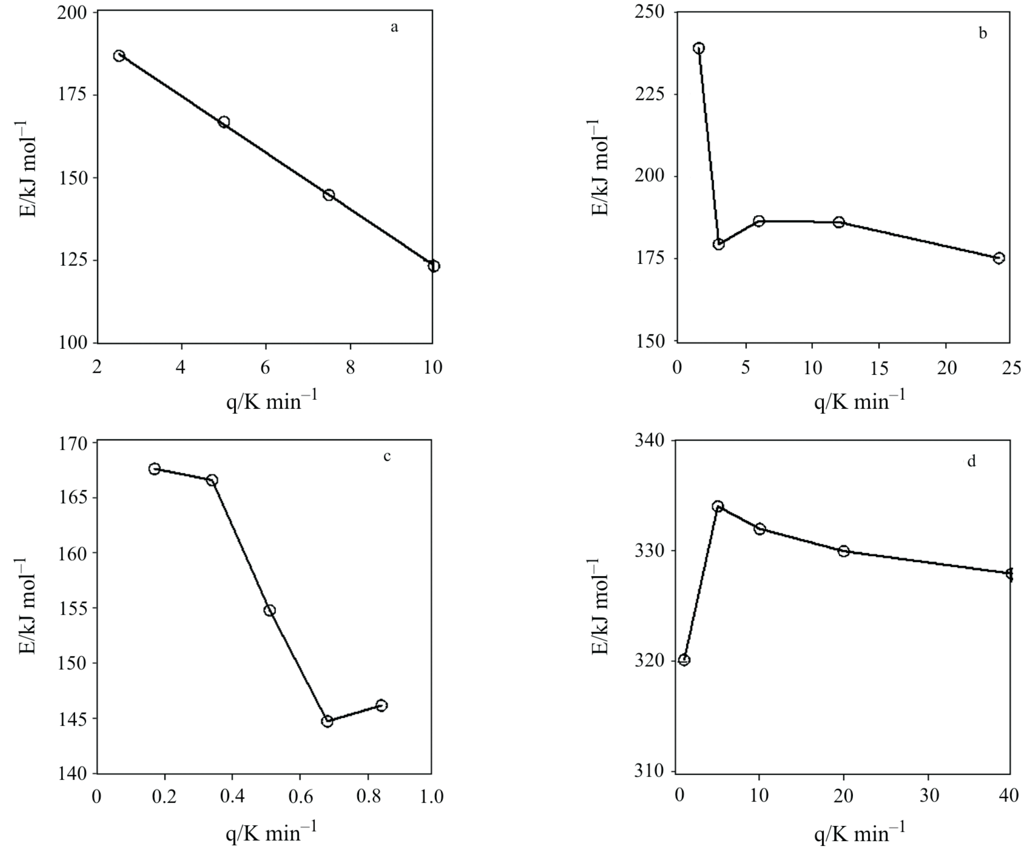

Fig. 1 Relationship of activation energy on heating rate for: a – dehydration reaction: $MnSO_4\cdot5H_2O\rightarrow MnSO_4\cdot3.25H_2O+1.75H_2O$ (model F1) [12], b – dehydration reaction: $CuSO_4\cdot3H_2O\rightarrow CuSO_4\cdot H_2O+2H_2O$ (model F1) [23, 24], c – decomposition of 1,3,5,7- tetranitro-1,3,5,7-tetrazocine (HMX) (power law) [25], d – dehydration reaction: $MnC_2O_4\cdot2H_2O\rightarrow MnC_2O_4+2H_2O$ (model A) [26]

tions, which contain Eyring Eq. (4) instead of Arrhenius one (1) (Table 1, No. 6 and 7). From suitable functions presented in Table 1 emerge searched relationships (12) and (14) connected by Eq. (15). It is necessary to stress that equation (Table 1, No. 6):

$$g(\alpha)=\frac{BT^2}{q}e^{-\Delta^+G/RT} \tag{16}$$

is a result of special case of integration of function containing temperature according to Błażejowski [13]; in other cases one obtains solution given in Table 1, No. 8, which follows from chosen approximation of Euler integral (Appendix B).

From Table 1 follows that relationship (12) is more connected with typical thermokinetic equation $g(\alpha)\sim T^2$ and Arrhenius and Kissinger laws and is multiplicity of Eq. (14), which is connected as well with thermokinetic equation $g(\alpha)\sim T$, as with Eyring equation. Forms of k_m depend on form of initial equation $g(\alpha)$ as well as from assumptions for differential thermokinetic equations $d\alpha/dT$.

Analysis of equations in Table 1 allows to conclude that reaction constants in temperature of maximal reaction rate are presented by 3 relationships: (2) as well as (12) and (14). Their analysis makes possible continuation of discussion presented in own works [16, 17] where authors concluded that using only kinetic parameters (E and A) is unreliable and does not bring unambiguous results. Only rate constant k_m connects together values of mentioned parameters and unambiguously informs about changes in reaction kinetics towards heating rate q. This is because k_m in version (12) or (14) follows from Kissinger law, which involves influence of heating rate q only by T_m without influence of E and A, which both behave different towards heating rate (Fig.1), what was proved in mentioned works [16, 17].

Arrhenius law and Eyring equation

Table 2 contains comparison of adequate kinetic (E and A) and thermodynamic (Δ^+H, Δ^+S and Δ^+G) quantities, from which follows that, with regard to equality of free energy, two couples of alternative dependencies exist:

$$\Delta^+H=E-RT_m,\quad \Delta^+S=R\left(\ln\frac{A}{T_m}-24.76\right) \tag{17}$$

Table 1 Interrelations between form of thermokinetic equation and reaction rate constant

No.	Function g(α) or $\frac{\mathrm{d}\alpha}{\mathrm{d}T}$	Condition	Reaction rate constant	Notes
1	$g(\alpha)=\frac{ART^2}{qE}\mathrm{e}^{-E/RT}$	1) $g(\alpha_m)=1$, $T=T_m$	$(k_m)_1=\frac{q}{T_m}\frac{E}{RT_m}$	No. (1) is approximation of solution No. 3
2	$g(\alpha)=k\frac{RT^2}{qE}$			
3	$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=f(\alpha)\frac{A}{q}\mathrm{e}^{-E/RT}$	2) $\mathrm{d}^2\alpha/\mathrm{d}T^2=0$, $T=T_m$, $\delta=1$ (Eq. (27) in [16])		
4	$g(\alpha)=\frac{AT}{q}\mathrm{e}^{-E/RT}$	1) $g(\alpha_m)=1$, $T=T_m$	$(k_m)_2=\frac{q}{T_m}$	–
5	$g(\alpha)=k\frac{T}{q}$	2) $\mathrm{d}^2\alpha/\mathrm{d}T^2=0$, $T=T_m$, $E/(E+RT_m)\cong 1$		Eqs (40), (41) in [16]
6	$g(\alpha)=\frac{BT^2}{q}\mathrm{e}^{\Delta^{+}S/R}\mathrm{e}^{-\Delta^{+}H/RT}$	$g(\alpha_m)=1$, $T=T_m$		g(α) acc. [13] when $k=C_1T\mathrm{e}^{-C_2/T}$ C_1, C_2=const
7	$g(\alpha)=k\frac{T}{q}$	–		
8	$g(\alpha)=\frac{BT^2}{2q}\mathrm{e}^{\Delta^{+}S/R}\mathrm{e}^{-\Delta^{+}H/RT}$	$g(\alpha_m)=1$, $T=T_m$	$(k_m)_2=\frac{2q}{T_m}$	–
9	$g(\alpha)=k\frac{T}{2q}$	–		

Table 2 Interrelations between enthalpy, entropy and free energy of activation

No.	Method of comparison	$\Delta^{+}H=$	$\Delta^{+}S^{a}$	$^{a)}\Delta^{+}G^{a}$
1	from derivative dln*k*/d*T*	$E-RT_m$, Eq. (8)	$R\left(\ln\frac{A}{T_m}-\ln B-1\right)$, Eq. (10)	$E+RT_m\left(\ln B-\ln\frac{A}{T_m}\right)$
2	Eqs (2) and (4) with (5)	E	$R\left(\ln\frac{A}{T_m}-\ln B\right)$	$E+RT_m\left(\ln B-\ln\frac{A}{T_m}\right)$
3	from relationship $\ln\frac{g(\alpha)}{T^2}$ (Table 1, No. 1 and 6)	E	$R\left(\ln\frac{AR}{E}-\ln B\right)$	$E+RT_m\left(\ln B-\ln\frac{AR}{E}\right)$
			$^{b)}R\left(\ln\frac{A}{T_m}-\ln B\right)-(22+R)^{b}$	$\cong E+RT_m\left(\ln B-\ln\frac{A}{T_m}\right)+T_m(22+R)\cong$ $\cong E+RT_m\left(\ln B-\ln\frac{A}{T_m}\right)$ $\Delta^{+}G>>T_m(22+R)$

$^{a}\ln B=23.76$

^{b}from correlation $R\left(\ln\frac{A}{T_m}-\ln B-1\right)=1.03R\left(\ln\frac{A}{T_m}-\ln B\right)+22$

or

$$\Delta^{+}H=E,\quad \Delta^{+}S=R\left(\ln\frac{A}{T_m}-23.76\right)\qquad(18)$$

because in both cases one obtains equality of $\Delta^{+}G$ according to Eq. (5).

Third considered case leads to approximated values (Table 2, No. 3) and we may pass it over. Thus, energy of activation is directly enthalpy of activation, taking assumptions given in the aim of the work and $T=T_m$.

Experimental

Thermogravimetric measures of thermal dissociation of $CuSO_4{\cdot}5H_2O$ and $CaC_2O_4{\cdot}H_2O$, as well as pyrolysis of PVC and high rank bituminous coal have been performed in dynamic nitrogen atmosphere and combustion of PVC and mixtures of electrographite with 3 chosen sodium silicates with different molar ratios have been performed in air. The inorganic compounds ($CuSO_4{\cdot}5H_2O$ and $CaC_2O_4{\cdot}H_2O$) have been chosen as model as thermal dissociation examples, while coal and PVC have been used as pyrolysis examples. Electrographite and its mixtures with sodium silicates have been chosen for investigations, because reactivity of graphite in the presence of inorganic compounds towards oxygen is very crucial from thermokinetic and technological point of view.

Thermogravimetric measures of all samples have been carried out on Mettler TG-50 thermobalance in TA-4000 thermoanalytic system. Samples have been heated in open Pt crucibles. Table 3 presents experimental conditions for each sample and Table 4 – characteristics of coal, electrographite and sodium silicate samples.

Verification of experimental data

There is graphical presentation of reaction rate constant *vs.* heating rate relationships presented on Fig. 2 for thermal dissociation of $CaC_2O_4{\cdot}H_2O$ (dehydration), described in work [27] and used again in work [16]. The described dehydration process fulfills as well relationship (11) as (13) and IE (6) for each heating rate used in thermogravimetric measures. Taking mentioned facts into consideration, values of k_m determined with help of Eq. (2) should fulfill inequality:

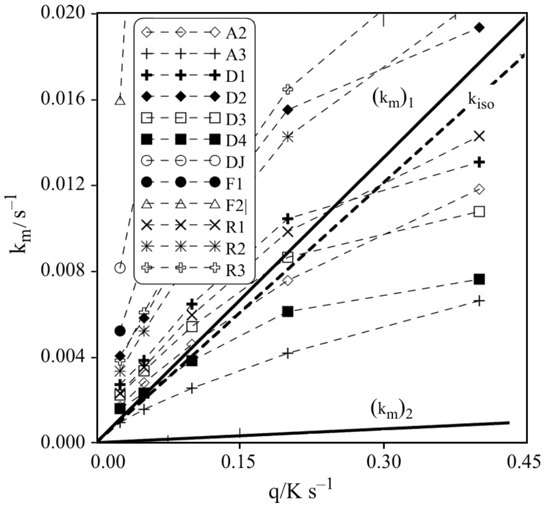

Fig. 2 Relationship of dehydration reaction rate: $CaC_2O_4{\cdot}H_2O \rightarrow CaC_2O_4 + H_2O$ acc. to Eq. (2) for different thermokinetic models and values of $(k_m)_1$, $(k_m)_2$ and k_{iso} on heating rate

$$(k_m)_1 \ge k_m \ge (k_m)_2 \quad \text{for } q=\text{var} \tag{19}$$

Eqs (12), (2) and (14), respectively.

The values of $(k_m)_1$, $(k_m)_2$ and k_{iso} have been calculated from Eqs (12), (14) and (6), respectively. The values of kinetic parameters (E and A) used in these equations have been determined from following relationships, respectively:

- Kissinger law in version (11) (for $(k_m)_1$),
- Kissinger law in version (13) (for $((k_m)_2)$,
- Arrhenius law (2), where values of E and A formed an IE, with the use of which the value of k_{iso} has been determined.

The relationship between $(k_m)_1$ and q (Eq. (12)) are in most cases rectilinear, but in a few cases the relationship has been found to be slightly curvilinear.

Table 3 Experimental conditions for each of analyzed sample

Sample	Sample mass, m/mg	Temperature range/°C	Furnace atmosphere	Gaz flow rate/mL min^{-1}	Heating rate, q/K min^{-1}
$CuSO_4{\cdot}5H_2O$	20	25–1100	N_2	200	1.5–3–6–12–24
$CaC_2O_4{\cdot}H_2O$		25–300		100	
PVC	10	180–380			
PVC			air		
electrographite		25–1100			6–12–24
electographite +30% $Na_2O{\cdot}SiO_2$					
electographite +30% $Na_2O{\cdot}2SiO_2$					
electographite +30% $Na_2O{\cdot}3.5SiO_2$					
bituminous coal	15		N_2		5–10–15–20–50

Table 4 Characteristics of coal, electrographite and sodium silicate samples

Sample	Molar ratio(SiO_2/Na_2O)	Bulk density/g cm^{-3}	Water insoluble/%	Fe_2O_3 /%
sodium metasilicate $Na_2O{\cdot}SiO_2$	1	1.02	0.3	0.02
sodium disilicate $Na_2O{\cdot}2SiO_2$	2	0.97	0.3	0.05
sodium silicate $Na_2O{\cdot}3.5SiO_2$	3.5	–	0.2	0.08
	Total moisture, W_t / %	Ash, A^d /%	Volatile matter, V^{daf}/%	Swelling Index, SI
electrographite	0.2	0.05	0.71	–
bituminous coal*	8.2	6.8	21.3	6.5

*Bituminous coal from Polish coal mine. Type 35.2B according to Polish Standard Classification of Coal

Values of kinetic parameters (E and A) have been determined with the use of Coats-Redfern relationship (Table 1, No. 1 and Table 5).

Analyzing Fig. 2 one may notice that not every kinetic model fulfills said condition for each of analyzed heating rates, except for models A3 and D4. Using both criterion $g(\alpha_m)=1$ [16, 17] and statistical one (r^2), the preferred model is R2, which still does not fulfill condition (19). Values of k_m increase together with heating rate, but slower than $(k_m)_1$, what leads to fulfillment of condition (19) for greater and greater amount of models (for $q=1.5$ K min^{-1} the condition (19) is fulfilled only by model A3, whereas for $q=24$ K min^{-1} – models A2, A3, D1, D3, D4 and R1). Such a behavior of constant k_m is not met in every case. However, using only models, which fulfill both criteria, statistical one and $g(\alpha_m)=1$, causes that dependencies k_m *vs.* q for selected models arrange themselves in various way towards straight-lines (12) and (14), but according to some rule, which we are going to discuss about further.

Analysis of all cases of thermal decomposition discussed in present work is reflected on Fig. 3, where distribution of reaction rate constants *vs*. heating rate according to Eqs (2), (12) and (14) are presented for models satisfying both criteria: $g(\alpha_m)=1$ and statistical one, for $q=6$, 12 and 24 K min^{-1}. One may draw following conclusions from Fig. 3:

A. We have 4 cases of k_m value behavior towards $(k_m)_1$ and $(k_m)_2$:

a) condition (19) is satisfied for all selected models – thermal dissociation (Fig. 3c), pyrolysis (Figs 3g, h) and combustion (Figs a, d); as we can see, in case of pyrolysis we have only one model satisfying criterion $g(\alpha_m)=1$ (Figs 3g, h), while dissociation of $CuSO_4{\cdot}H_2O$ (Fig. 3c) – three ones,

b) values of k_m oscillate around $(k_m)_1$, reaching greater or lower $g(\alpha_m)=1$ values: $k_m\approx(k_m)_1$ – for ‘three-model’ cases (where 3 models have been selected) – Figs 3a, d, e (exception: Fig. 3c) and Fig. 4c,

c) values of k_m are greater than $(k_m)_1$: $k_m>(k_m)_1$ – Fig. 3f and Figs 4b, e,

d) one secluded case for thermal dissociation, where $k_m<<(k_m)_2$ – Fig.3 b;

B. We have 2 cases of k_{iso} value behavior towards $(k_m)_1$ and $(k_m)_2$:

a) for processes of thermal dissociation (Figs 3c, e, f), pyrolysis (Figs 3g, h) and combustion (Fig. 4 – all cases) k_{iso} satisfies condition $(k_m)_1\geq k_{iso}\geq(k_m)_2$

b) for thermal dissociation processes, for which 3 models have been selected, then: $k_{iso}>(k_m)_1$ (Figs 3a, d).

Such different behavior of k_m and k_{iso} towards rectilinear relationships (12) and (14) follows from mutual relations between kinetic parameters determined from Kissinger law (11) and (13) and IE (6) (or more specifically: the point of intersection of straight-lines ln$A$ *vs.* E for individual heating rates (Fig. 4). For all analyzed cases, points $P_I(\ln A_I,E_I)$ – Eq. (11) and $P_{II}(\ln A_{II},E_{II})$ – Eq. (13) are located around the intersection point, P. Comparing dependencies k_m *vs.* q (Figs 3a-h and Figs 4a-e) with corresponding IE relationships (Figs 3i–p and Figs 4f–j), one may conclude:

case A-a corresponds to the following situations (E_P – value of activation energy in point P):

- $E_p>E_I$, E_{II} – for inert atmosphere processes: thermal dissociation (Fig. 3k) and pyrolysis (Figs 3o, p),
- $E_p<E_I$, E_{II} – for combustion – Figs 4f, i,

case A-b (area 1 on Fig. 5)

- $E_p\approx E_I$, E_{II} – thermal dissociation (Figs 3i, l, m) and combustion (Fig. 4h),

Table 5 Comparison between relationships by means of which determined kinetic parameters are dependent or independent on heating rate – examples from literature

Equation/method	Obtained kinetic parameters	Literature
Kissinger law: $\ln\frac{q}{T_m^2}=\ln\frac{AR}{E}-\frac{E}{RT_m}$, $E=E_I$, $A=A_I$	E, A=const. for q=var $E_I\neq E_{II}$, $A_I\neq A_{II}$	[16, 17, 22, 25]
Kissinger law in modified form: $\ln\frac{q}{T_m}=\ln A-\frac{E}{RT_m}$, $E=E_{II}$, $A=A_{II}$		[16, 17]
Kissinger-Akahira-Sunose (KAS) method: $\ln\frac{q}{T_\alpha^2}=\ln\frac{AR}{Eg(\alpha)}-\frac{E}{RT_\alpha}$, $E=E_\alpha$, $A=A_\alpha$	Isoconversional methods E, A = const. for q = var and α = const. kinetic parameters do not depend on heating rate, but depend on α; E varies with α; A is determined e.g. by the use of IE or Kinetic Compensation Effect (KCE) [35]	[29]
Flynn-Wall-Ozawa (FWO) method in version: $\ln q=\ln\frac{AE}{Rg(\alpha)}-5.331-1.052\frac{E}{RT_\alpha}$ for $20<\frac{E}{RT}<60$, $E=E_\alpha$, $A=A_\alpha$		[29, 37]
Friedman's method: $\ln\left(q\frac{d\alpha}{dT}\right)=\ln Af(\alpha)-\frac{E}{RT}$, $E=E_\alpha$, $A=A_\alpha$		[29, 36, 37]
Coads-Redfern method (comp. Table 1, No.1 and Table 2, No. 3): $\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{qE}-\frac{E}{RT}$	Model-fitting methods E, A = var for q = var and $g(\alpha)$ = var	[16, 17] [29, 38–40]
'General method' (comp. Table 1, No.4): $\ln\frac{g(\alpha)}{T}=\ln\frac{A}{q}-\frac{E}{RT}$		[16, 17]
Kinetic compensation effect (KCE)/isokinetic effect (IE)/invariant kinetic parameters method (IKP): $\ln A=a+bE$, q = var	Kinetic parameters obtained by model-fitting methods are intercorrelated, forming rectilinear relationships for each heating rate. The relationships intersect at (nearly) one point that corresponds to true values of A and E – the so-called invariant kinetic parameters (E_{inv}, A_{inv} or E_P, A_P), which are independent on heating rate: E_{inv}, A_{inv} or E_P, A_P = const. for q = var	[16, 17, 28, 29]

case A-c

- $E_p<E_I$, E_{II} – thermal dissociation (Fig. 3f)
- $E_p>E_I$, E_{II} – combustion (Figs 4g, j),

case A-d (area 2 on Fig. 5):

- $P_I\approx P_{II}$, and $E_P\approx 0$, Fig. 3j,

case B-a:

- E_I, $E_{II}\neq E_p$ – Figs 3k, n-p (exception: Fig. 3m) and Figs 4f, g, i, j (exception: Fig. 4c),

case B-b:

- E_I, $E_{II}\approx E_p$ – Figs 3i, l.

Analysis of location of the points, which coordinates are values of kinetic parameters E and A determined from Eqs (11) and (13), towards IE allows capturing significant differences in kinetics of processes taking place in inert (pyrolysis and thermal dissociation) and oxidizing (combustion) atmosphere. While k_m (Eq. (2)) approaches $(k_m)_2$, then for oxygen-free processes we may notice decreasing of value of activation energy (E_P) and its approaching towards values of E_I (Eq.(11)) or E_{II} (Eq. (13)), while for combustion – increasing of E_P is observed. This tendency is also valid in opposite situation. Decrease of k_m value below $(k_m)_2$ causes further decreasing of E_P for thermal dissociation and pyrolysis and increasing for combustion. On the other hand, when k_m reaches $(k_m)_1$ (for 'three-model' cases – Figs 3a, d, e and Fig. 4c), then $E_P=E_I$ or E_{II}. Reaching minimal values of k_m (Fig. 3b)

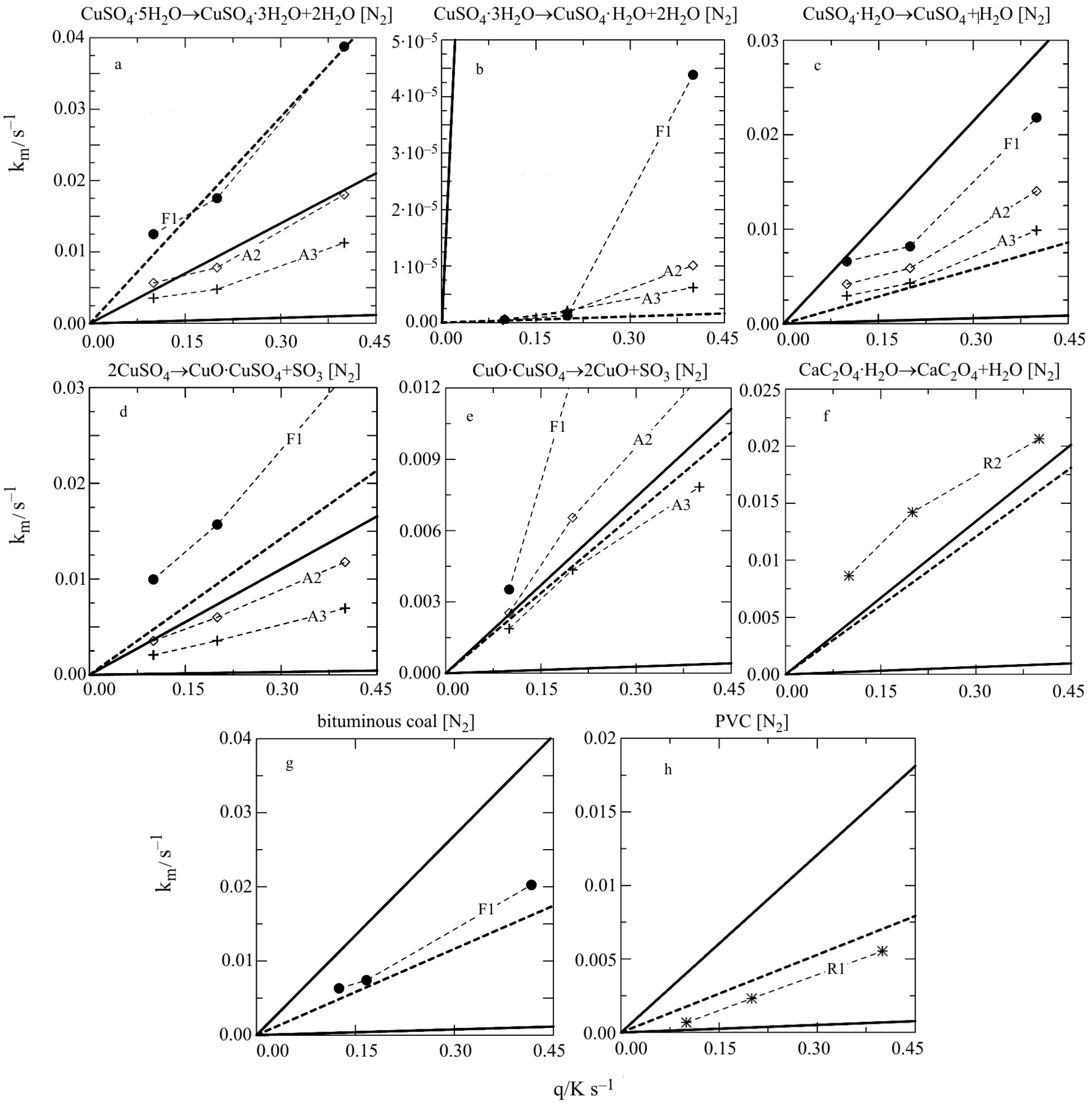

Fig. 3 Reactions of thermal dissociation analyzed in present work. a–h: Relationship of rate constant k_m and k_{iso} on heating rate on the background of straight-lines (12) and (14). Key the same as on Fig. 2

finds its reflection in minimal values of E_P (Fig. 3j), however this conclusion is based only on one case of thermal dissociation. Basing on said analyses, one may suppose that for combustion we can expect opposite situation, i.e. maximal values. Figure 5 recapitulates above discussion.

The reasons of such location of pairs of kinetic parameters forming coordinates of points P_I, P_{II} and P follow from the following fact: straight-lines of IE for all heating rates intersect in (nearly) one point P, in which kinetic parameters are the same for each heating rate, thus they are independent on q. The fact was also mentioned, among others, by Lesnikovich and Levchik [28] as well as by Budrugeac and Segal [29]. Independence on q is also characteristic for kinetic parameters determined from two forms of Kissinger law (11) and (13), which result from some kind averaging of kinetic parameters for q=var. The points P_I, P_{II} and P depend only on values of kinetic parameters E and A, without influence of temperature T_m (because T_m increases together with q), which is included in reaction rate constant equations. The fact manifests itself in similar behavior of k_m *vs.* q relationship (e.g. Fig. 3h and Fig. 4a), while in ln$A$ *vs.* E system we can see opposite behavior (e.g. Fig. 3p and Fig. 4f). As we can see the obtained kinetic parameters depend or are independent on heating rate. There are some examples of non-isothermal kinetic methods in Table 5, which represent dependence or independence of evaluated kinetic parameters on heating rate.

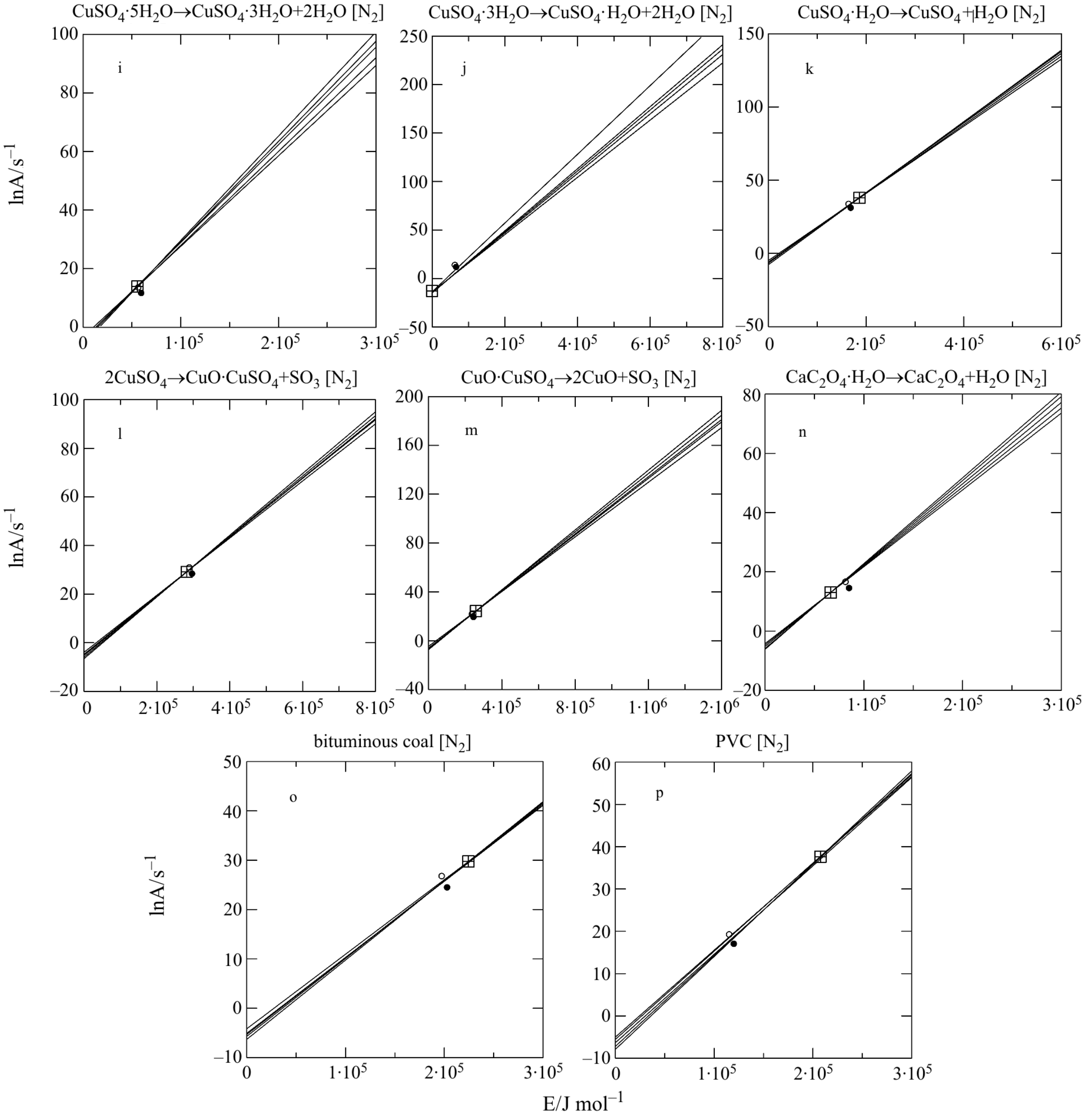

Fig. 3 cont. Reactions of thermal dissociation analyzed in present work. i–p: Location of point P [+] of intersection of IE (6) straight-lines for different heating rates towards points P_I (○) and P_{II} (●)

Therefore, scattering of k_m values determined with the use of Eq. (2) depending on heating rate, follows from the fact of unfulfillment of assumption of kinetic parameters (E and A) invariability towards heating rate. On the other hand, obtained values of E and A for different thermokinetic models are characterized by their large scattering, oscillating around average and, in spite of the fact that they satisfy IE, the latter is blurred (as it was presented previously [18, 26]). Heating rate variability influences changes of slope of ln$A$ *vs*. E rectilinear relationship in very subtle way or rather imperceptible in categories of statistical analyses, what is undoubtedly connected with relationship [16]:

$$\frac{\partial \ln A}{\partial E} = \frac{1}{RT_m}, \quad T_m = f(q) \tag{20}$$

We can not precisely say on the basis of above analyses, at what heating rate thermogravimetric measures of thermal decomposition of solids should be carried out, because precision in heating rate values partition does not exist. Instead, we may distinguish two ranges of heating rate values, for which the partition can be made:

- $q<10$ K min^{-1}, where behavior of kinetic quantities (E, A, k_m) is chaotic and unpredictable (Figs 1b and 2),
- $q>10$ K min^{-1}, where relationship between q and E, A, k_m is either rectilinear or invariable towards q according to condition (11) or (13).

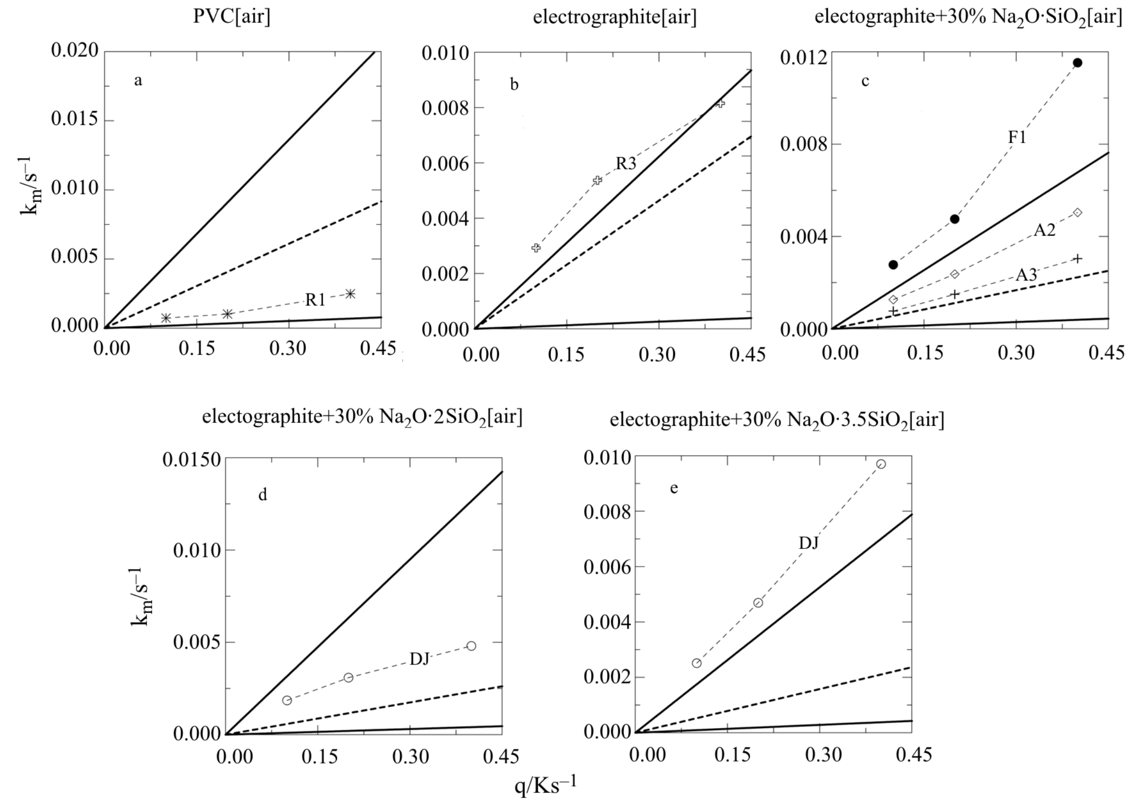

Fig. 4 Reactions of combustion analyzed in present work. a–e: Relationship of rate constant k_m and k_{iso} on heating rate on the background of straight-lines (12) and (14). Key the same as on Fig. 2

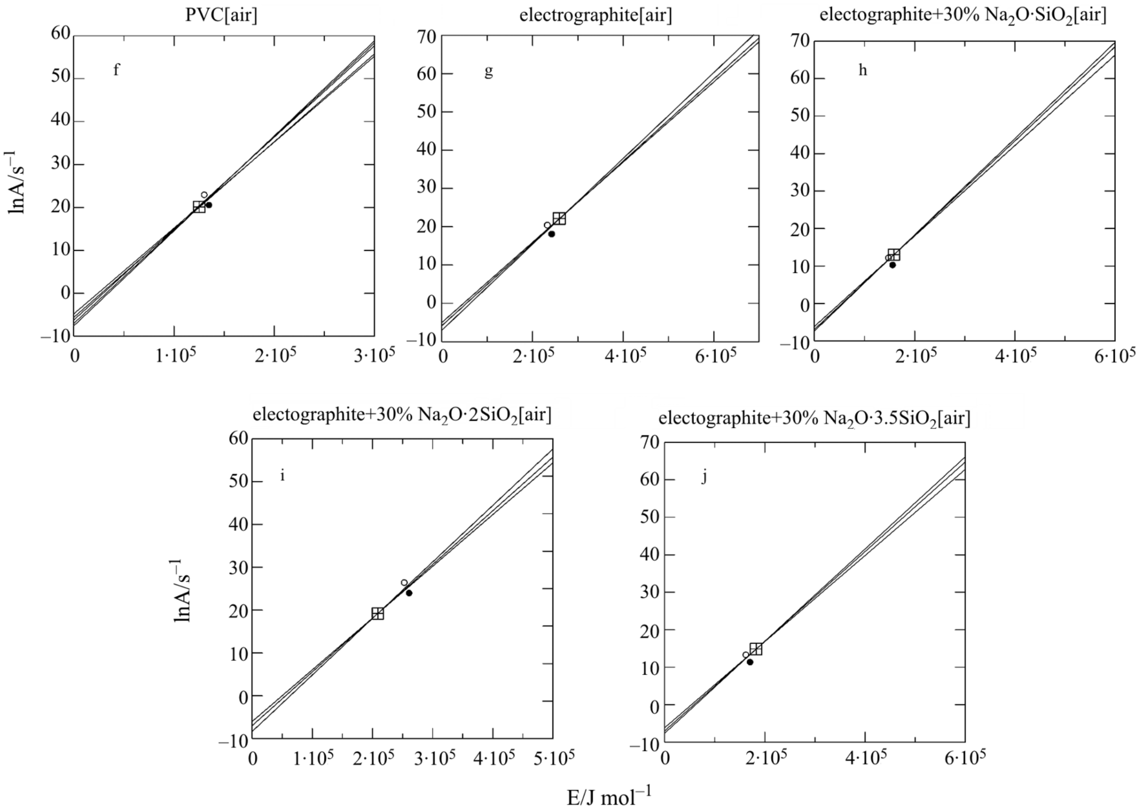

Fig. 4 cont. Reactions of combustion analyzed in present work. f–j: Location of point P [+] of intersection of IE (6) straight-lines for different heating rates towards points P_I (❍)and P_{II} (●)

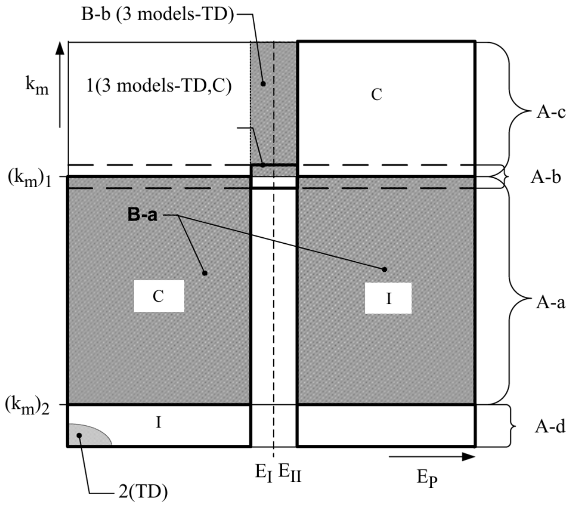

Fig. 5 Simplified scheme recapitulating relations between behavior of k_m towards $(k_m)_1$ and $(k_m)_2$ and E_P towards E_I and E_{II}. Comment in the text. (C – combustion, I – inert atmosphere processes, TD – thermal dissociation)

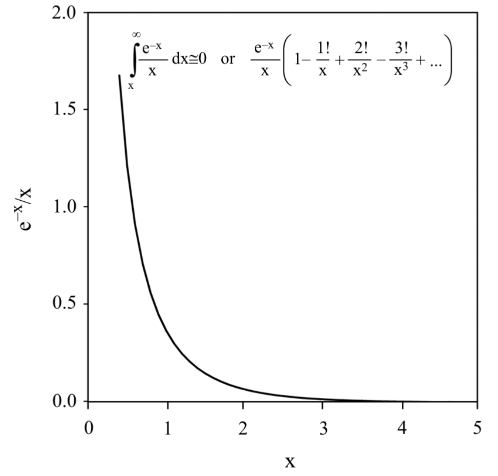

Fig. 6 Course of integrated function in Euler's integral

Conclusions

In thermal decomposition of solids Eyring equation is an element connecting used thermokinetic equations $g(\alpha)$ for two most justified versions (No. 1 and 4 in Table 1), which contains Arrhenius law. In the same time Eyring law points to validity of consideration of thermokinetic quantities (in dynamic conditions) in way relative for 3 kinetic rate constants (k_m, $(k_\mathrm{m})_1$ and $(k_\mathrm{m})_2$) according to Eq. (2) and Eqs (12) and (14).

Kinetic rate constants k_m, $(k_\mathrm{m})_1$ and $(k_\mathrm{m})_2$ result from different laws (Arrhenius' and both Kissinger's), therefore we may expect their different arrangement towards q. Using values of kinetic parameters (resulted from different thermokinetic models) in Arrhenius equation (2) gave chaotic behavior of k_m towards q (Fig. 2). Therefore, without using statistical criterion and $g(\alpha_\mathrm{m})=1$ one can not say, which model is appropriate for analyses of thermal processes. Analysis of k_m *vs.* q with the use of both mentioned criteria and Kissinger law ($(k_\mathrm{m})_1$ and $(k_\mathrm{m})_2$) allow to show differences between kinetics of inert and oxidizing atmosphere processes (Figs 3a-h and Figs 4a-e). The differences are consistent with IE for different heating rates towards Kissinger law (Figs 3i-p and Figs 4f-j). As well kinetic rate constant as isokinetic behavior are interdependent, what is presented on Fig. 5.

Analysis of quantities other than k_m, i.e. E, A, Δ^+H, Δ^+S towards heating rate is an incomplete method and does not lead to unambiguous conclusions, which make possible answering the question, at what heating rate thermokinetic analysis is most justified.

Values of k_m according to Eqs (2) and (4) (identity) should be located within range defined by rectilinear relationships (12) – maximum, and (14) – minimum, for thermal processes carried out in dynamic conditions (q=var), assuming that E and A are invariable towards q and satisfy Kissinger law in two versions: (11) and (13). However, there might be some deviation caused by:

- Reaction rate constant k_iso in Eq. (6) is invariant in sense of statistical defining of free term in equation reduced to linear form. But in practice, using both Eq. (2) and assumption (7), pairs of parameters E and A for particular models $g(\alpha)$ lead to variable numerical values, which oscillate around average (Fig. 2). IE is very often blurred (comp. [18, 30]).
- Invariability of E and A towards q is not conserved.

It was concluded that thermogravimetric measurements carried out at different heating rates is justified from point of view of kinetic analysis of thermal decomposition. At low heating rates (below 10 K min^{-1}) quantities developed from thermokinetic calculations behave somewhat different from those obtained at higher heating rates (over 10 K min^{-1}). In result, we get two sets of information about process kinetics. In case of isoconversional methods at least three heating rates are enough in order to present the full kinetic picture of the process [31]. At the same time, using classic model-fitting kinetics methods two thermogravimetric measurements at low and high heating rate are the minimum, which are necessary for this purpose.

Appendix A

In Eq. (16) using $g(\alpha_\mathrm{m}) = 1$ for $T = T_\mathrm{m}$ we obtain:

$$\Delta^+G = RT_\mathrm{m}\ln\frac{BT_\mathrm{m}^2}{q} \quad \text{(A1)}$$

From Kissinger law in version (11) we have:

$$\frac{T_\mathrm{m}^2}{q}=\frac{E}{AR}\mathrm{e}^{\mathrm{E/RT_m}} \tag{A2}$$

and

$$\Delta^+G=E+RT_\mathrm{m}\left(\ln B+\ln\frac{E}{AR}\right) \tag{A3}$$

Using modified version (13) we obtain:

$$\frac{T_\mathrm{m}}{q}=\frac{\mathrm{e}^{\mathrm{E/RT_m}}}{A} \tag{A4}$$

and

$$\Delta^+G=E+RT_\mathrm{m}\left(\ln B+\ln\frac{T_\mathrm{m}}{A}\right) \tag{A5}$$

According to Table 2 relationship (A3) is approximation of (A5). For obvious relation $E>RT_\mathrm{m}$ one may obtain inequality:

$$\Delta^+G(\mathrm{A1})\cong\Delta^+G(\mathrm{A3})>\Delta^+G(\mathrm{A5}) \tag{A6}$$

From relationship (A1) follows that Δ^+G depends on increasing values of q and T_m. According to (A5), while E and A=idem, then Δ^+G depends on A and T_m in following way:

$$\Delta^+G=E+\left(R\ln\frac{B}{A}\right)T_m+RT_\mathrm{m}\ln T_m \tag{A7}$$

However, to all intents and purposes, even for relation $B<A$ the second term is much lower than the third one, thus Δ^+G increases with increasing T_m, what also has been proved using correlation analysis [12]. Variability of Δ^+G *vs.* q is insignificant.

Appendix B

Let's introduce formula (3) into equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{k}{q}f(\alpha) \tag{B1}$$

to obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{BT}{q}\mathrm{e}^{-\Delta^+\mathrm{G/RT}}f(\alpha) \tag{B2}$$

After integration with using Eq. (5) we obtain:

$$g(\alpha)=\frac{B}{q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\int_0^\mathrm{T}T\mathrm{e}^{-\Delta^+\mathrm{H/RT}}\mathrm{d}T \tag{B3}$$

Let's substitute:

$$\frac{\Delta^+H}{RT}=x,\quad T=\frac{\Delta^+H}{Rx},\quad \mathrm{d}T=-\frac{\Delta^+H}{R}\frac{\mathrm{d}x}{x^2} \tag{B4}$$

thus

$$g(\alpha)=\frac{B}{q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\left(\frac{\Delta^+H}{R}\right)^2\int_\mathrm{x}^\infty\mathrm{e}^{-x}\frac{\mathrm{d}x}{x^3} \tag{B5}$$

We solve the integral in (B5) using fragmentary integration [32]

$$\int_\mathrm{x}^\infty\mathrm{e}^{-x}\frac{\mathrm{d}x}{x^3}=\frac{\mathrm{e}^{-x}}{2x^2}-\frac{\mathrm{e}^{-x}}{2x}+\frac{1}{2}\int_\mathrm{x}^\infty\frac{\mathrm{e}^{-x}}{x}\mathrm{d}x \tag{B6}$$

Next, we may treat the Euler's integral in following way (Fig. 6):

$$Ei(-x)=\int_\mathrm{x}^\infty\frac{\mathrm{e}^{-x}}{x}\mathrm{d}x\cong0 \tag{B7}$$

or [33, 34]

$$\begin{aligned}Ei(-x)&=\int_\mathrm{x}^\infty\frac{\mathrm{e}^{-x}}{x}\,\mathrm{d}x=\frac{\mathrm{e}^{-x}}{x}\left(1-\frac{1!}{x}+\frac{2!}{x^2}+\frac{3!}{x^3}+\ldots\right)=\\&=\frac{\mathrm{e}^{-x}}{x}\left(1-\frac{1}{x}\right)\end{aligned} \tag{B8}$$

or

$$Ei(-x)\cong\frac{\mathrm{e}^{-x}}{x} \tag{B9}$$

Finally, the Euler's integral may be approximated in three ways

$$Ei(-x)\cong0,\ Ei(-x)\cong\frac{\mathrm{e}^{-x}}{x}\left(1-\frac{1}{x}\right),\text{ and }Ei(-x)\cong\frac{\mathrm{e}^{-x}}{x} \tag{B10}$$

Conclusively, (B5) is presented as:

$$g(\alpha)=\frac{B}{q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\left(\frac{\Delta^+H}{R}\right)^2\frac{\mathrm{e}^{-x}}{2x}\left(\frac{1}{x}-1\right)\le0\qquad(x\ge1) \tag{B11}$$

$$g(\alpha)=\frac{B}{q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\left(\frac{\Delta^+H}{R}\right)^2\cdot0=0 \tag{B12}$$

$$g(\alpha)=\frac{B}{q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\left(\frac{\Delta^+H}{R}\right)^2\frac{\mathrm{e}^{-x}}{2x^2} \tag{B13}$$

and after all

$$g(\alpha)=\frac{BT^2}{2q}\mathrm{e}^{\Delta^+\mathrm{S/R}}\mathrm{e}^{-\Delta^+\mathrm{H/R}T} \tag{B14}$$

The solution (B14) differ from Eq. (16) in value of coefficient 1/2.

Nomenclature

A	pre-exponential factor in Arrhenius equation (s^{-1}),
a	intercept of ln$A$ *vs*. E relationship (Table 5),
α	conversion degree, $0\le\alpha\le1$,
b	slope of ln$A$ *vs*. E relationship (Table 5),
Δ^+G	free energy of activation (J mol^{-1}),
Δ^+H	enthalpy of activation (J mol^{-1}),
Δ^+S	entropy of activation (J mol^{-1} K^{-1}),
E	activation energy (kJ mol^{-1} or J mol^{-1}),
$g(\alpha)$	mass integral,
h	Planck's constant, $h=6.626169\cdot10^{-34}$ (J s),
IE	isokinetic effect,
k	reaction rate constant (s^{-1}),
k_B	Boltzmann's constant, $k_\mathrm{B}=1.380622\cdot10^{-23}$ (J K^{-1}),

m	sample mass (mg),
q	heating rate (K s^{-1} or K min^{-1}),
R	gas constant, $R = 8.314$ J mol^{-1} K^{-1},
r^2	determination coefficient for linear regression; $0 \le r^2 \le 1$,
T	temperature (K),
τ	time (s).

Subscripts:

1, 2	denotes k_m determined from relationship (11) or (13), respectively,
α	denotes relationship on conversion degree in isoconversional methods (Table 5),
I	denotes E and A for Kissinger law in version (11),
II	denotes E and A for Kissinger law in version (13),
iso	isokinetic point,
inv	denotes invariant kinetic parameter (Table 5),
m	maximum rate of the process,
P	denotes invariant kinetic parameter.

References

1 D. Vamvuka, E. Kastanaki, M. Lasithiotakis and C. Papanicolaou, Carbon, 42 (2004) 351.
2 El-H. M. Diefallah, M. A. Gabal, A. A. El-Bellihi and N. A. Eissa, Thermochim. Acta, 376 (2001) 43.
3 J. A. Conesa, J. A. Caballero and J. A. Reyes-Labarta, J. Anal. Appl. Pyrol., 71 (2004) 343.
4 I. Martin-Gullon, M. Esperanza and R. Font, J. Anal. Appl. Pyrol., 58–59 (2001) 635.
5 M. A. Gabal, A. A. El-Bellihi and S. S. Ata-Allah, Mater. Chem. Phys., 81 (2003) 84.
6 A. Aouad, M. Benchanâa, A. Mokhlisse and A. Ounas, J. Therm. Anal. Cal., 75 (2004) 887.
7 R. E. White, P. S. Thomas, M. R. Phillips and R. Wuhrer, J. Therm. Anal. Cal., 80 (2005) 237.
8 D. V. Bavbande, R. Mishra and J. M. Juneja, J. Therm. Anal. Cal., 78 (2004) 775.
9 M. L. A. Gonçalves, D. A. Pinto da Mota, A. M. R. F. Teixeira and M. A. G. Teixeira, J. Therm. Anal. Cal., 80 (2005) 81.
10 H. Barkia, L. Belkbir and S. A. A. Jayaweera, J. Therm. Anal. Cal., 76 (2004) 623.
11 P. W. Atkins, Physical Chemistry, 6th Ed., Oxford University Press, Oxford–Melbourne–Tokyo, 1998.
12 M. Olszak-Humienik and J. Możejko, Thermochim. Acta, 405 (2003) 171.
13 J. Błażejowski, Thermochim. Acta, 48 (1981) 109.
14 J. Straszko, M. Olszak-Humienik and J. Możejko, Inż. Chem. Procesowa, 1 (1995) 45.
15 F. Tudos and P. K. David, Polym. Degrad. Stab., 50 (1995) 159.
16 A. Mianowski, J. Therm. Anal. Cal., 74 (2003) 953.
17 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 75 (2004) 355.
18 A. Mianowski and T. Radko, Pol. J. Appl. Chem., 38 (1994) 395.
19 L. T. Vlaev, I. G. Markovska and L. A. Lyubchev, Thermochim. Acta, 406 (2003) 1.
20 J. Pająk and Ł. Socha, Fuel Process. Technol., 77–78 (2002) 131.
21 J. Pająk and Ł. Socha, Energy Fuels, 19 (2005) 348.
22 W. W. Wentlandt, Anal. Chim. Acta, 27 (1962) 315.
23 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 74 (2003) 423.
24 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 74 (2003) 433.
25 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340-341 (1999) 53.
26 X. Gao, D. Chen and D. Dollimore, Thermochim. Acta, 215 (1993) 83.
27 A. Mianowski and T. Radko, Thermochim. Acta, 247 (1994) 389.
28 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 27 (1983) 89.
29 P. Budrugeac and E. Segal, Int. J. Chem. Kinet., 33 (2001) 564.
30 M. Owczarek and A. Mianowski, The influence of oxygen upon reactivity of chars in the presence of steam, Ed. WSKKTechChem, Gliwice 2000.
31 M. Maciejewski, Thermochim. Acta, 355 (2000) 145.
32 I. M. Ryżyk and I. S. Gradsztejn, Tablice całek, sum, szeregów i iloczynów (Tables of Integrals, Sums, Series, Products), PWN, Warszawa, 1964, Eq. (2. 325) (in Polish).
33 A. Mianowski and T. Radko, Thermochim. Acta, 204 (1992) 281.
34 J. Šesták, Thermochim. Acta, 3 (1971) 150.
35 S. Vyazovkin and C. A. Wight, Annu. Rev. Phys. Chem., 48 (1997) 125.
36 P. Budrugeac and E. Segal, Thermochim. Acta, 260 (1995) 75.
37 D. Zhan, C. Cong, K. Diakite, Y. Tao and K. Zhang, Thermochim. Acta, 430 (2005) 101.
38 J. M. Criado, J. Morales and V. Rives, J. Thermal Anal., 14 (1978) 221.
39 J. M. Criado and J. Morales, Thermochim. Acta, 19 (1977) 305.
40 N. Koga and H. Tanaka, J. Thermal Anal., 34 (1988) 177.

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