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The possibility of identification of activation energy by means of the temperature criterion

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Abstract

The influence of the selection of the $f(\alpha)$ function, which represents the reaction/process mechanism, on the values of the resulting kinetic parameters is discussed. It has been found that the solutions, in the form of the Arrhenius equation constants, show an isokinetic effect over a wide range of temperature. A special relationship between α (degree of conversion), E and T holds for low values of degree of conversion.

Keywords: Activation energy; Coal; Degree of conversion; DTG; Isokinetics; Mechanism; Polymer; Temperature criterion

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List of symbols

A	pre-exponential factor/min^{-1} in the Arrhenius equation
A	substrate of reaction
B,C	products of reaction
e	Euler's number, $e = 2.718\ldots$
E	activation energy/kJ mol^{-1}
$f(\alpha)$	function symbol of the argument α
$g(\alpha)$	weight integrals
m	mass of the sample/mg
$m(T)$	mass/mg of the sample at temperature T

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N	number of measurements (excluding the points $\alpha = 0$ and $\alpha = 1$)
n	order of reaction; in Eq. (14), number of moles
q	rate of heating/K min^{-1}
R	universal gas constant, $R = 0.008314$ kJ mol^{-1} K^{-1}
$r^2(\rho^2)$	linear determination coefficient (for straight line crossing point with coordinates (0,0))
T	absolute temperature/K
T_m	temperature at the maximal reaction rate/K
T_D	temperature at $\alpha_D = 0$/K
α	degree of conversion, $\alpha \in \langle 0,1 \rangle$

Subscripts

D	diffusion range
f	final
g	gas
i	initial
K	kinetic range
m	at the T_m temperature
s	solid

1. Introduction

Assuming the legitimacy of the classic kinetic equation for non-isothermal (dynamic) conditions

$$\frac{d\alpha}{dT} = \frac{A}{q} f(\alpha) e^{-E/RT} \tag{1}$$

where $\alpha \in \langle 0,1 \rangle$ and $q = \text{idem} > 0$. At the same time

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{2}$$

It has been shown previously [1] that at least two approximations can be derived from Eq. (1) resulting from the general form of the weight integral $g(\alpha)$

$$g(\alpha) = \frac{ART^2}{qE} e^{-E/RT} \tag{3}$$

and

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

According to Ref. [2], the pre-exponential factor of the Arrhenius equation A in Eq. (4) for the function

$$f(\alpha) = (1 - \alpha)^n \qquad n \geq 0 \tag{5}$$

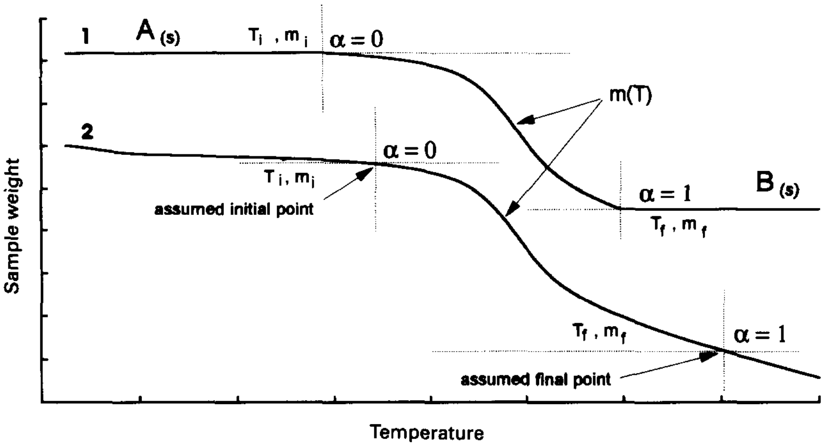

Fig. 1. Conversion degree for: curve 1, complete and irreversible conversion; curve 2, complex conversion of high molelcular weight substance.

(n is reaction order) can be evaluated from the equation

$$A = \frac{qE}{RT_m^2} e^{E/RT_m} \tag{6}$$

The conversion degree used in analyses is a kinetic parameter defined as (Fig. 1)

$$\alpha = \frac{m_i - m(T)}{m_i - m_f} \tag{7}$$

where m is sample weight, the subscripts i and f are the initial and final conditions, respectively, and $m(T)$ is the sample weight at temperature T.

Sometimes the supplementary parameter T_m (the temperature of the maximal reaction rate) in Eq. (4) enables the reaction order to be established. For the function $f(\alpha)$ defined by Eq. (5), provided that $T = T_m$, the following equations are obtained

$$\alpha_m = 1 - n^{1/(1-n)} \qquad \text{for } n \neq 1 \tag{8}$$

and

$$\alpha_m = 1 - e^{-1} = 0.632 \qquad \text{for } n = 1 \tag{9}$$

In the data from the literature, the $f(\alpha)$ function takes on various forms depicting the reaction mechanisms. A generalized equation including all these forms is [3–11]

$$f(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{10}$$

For specific values of the m, n and p parameters, the appropriate mechanisms are labelled as shown in Table 1. Some other authors recognize a strictly empirical nature in the above mentioned parameters [12], extracting no information from them on the reaction mechanism.

Table 1
Mechanism labels and mathematical form of the $f(\alpha)$ and $g(\alpha)$ functions according to Ref. [5]

Mechanism label	$f(\alpha)$	$g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$
Fn, $n > 1$	$(1-\alpha)^n$	$\frac{1-(1-\alpha)^{1-n}}{1-n}$
F1 ($n = 1$)	$1-\alpha$	$-\ln(1-\alpha)$
R1	$(1-\alpha)^0 \equiv 1$	α
R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
D1	α^{-1}	$\alpha^2/2$
D2	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
D3	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$
D4	$[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}\left[1-\frac{2\alpha}{3}-(1-\alpha)^{2/3}\right]$

For the chemical reaction of the general scheme

$$\mathrm{A(s)} \rightarrow \sum \mathrm{B(s)} + \sum \mathrm{C(g)} \tag{11}$$

or

$$\mathrm{A(s)} \rightarrow \sum \mathrm{C(g)} \tag{12}$$

the conversion degree referred to the substrate A may be formulated as its mass loss

$$\alpha = 1 - \left[\frac{m_\mathrm{A}(T)}{m_\mathrm{A,i}}\right] \qquad \mathrm{d}\alpha = \frac{-\mathrm{d}m_\mathrm{A}(T)}{m_\mathrm{A,i}} \tag{13}$$

or as the mole loss of A

$$\alpha = 1 - \left[\frac{n_\mathrm{A}(T)}{n_\mathrm{A,i}}\right] \qquad \mathrm{d}\alpha = \frac{-\mathrm{d}n_\mathrm{A}(T)}{n_\mathrm{A,i}} \tag{14}$$

if the molecular weight of substrate A is known.

When analysing solid conversions on the basis of thermogravimetric results, one can anticipate that the assumed mechanism of the $f(\alpha)$ conversion, represented in Eqs. (3) and (4) by the weight integral $g(\alpha)$, would influence the estimated kinetic parameters, i.e. the activation energy E and frequency constant A in the Arrhenius equation. It can also be anticipated that the parameters determined would satisfy the isokinetic effect formulated in linear form [1,12–19]

$$\ln A = a + bE \tag{15}$$

and in particular [1]

$$\frac{\partial \ln A}{\partial E} = \frac{1}{RT_m} \tag{16}$$

The aim of this paper is to prove that by assuming the different conversion mechanisms in Eqs. (3) and (4) (see Table 1) kinetic parameters which show an isokinetic effect result (Eqs. (15) or (16)).

Previous work [1] showed that when selecting just one $f(\alpha)$, i.e. $f(\alpha) = (1-\alpha)^n$ with a variety of values of n, one obtains kinetic parameters showing an isokinetic effect. In that particular case the isokinetic effect occurred over a narrow range of $\ln A$ and E values, as compared with the experiments based on the interpretation of data extracted from Ref. [12].

In the present study, a thermogravimetric analysis for the dehydration of calcium oxalate monohydrate is reported

$$CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g) \tag{17}$$

This compound was chosen because many authors have studied the kinetics of its transformations under various conditions, for example Refs. [10,20–34]. A comparison of the kinetic parameters extracted from the above papers shows that the activation energy of reaction (17) changes crucially depending upon the mechanism assumed, ranging from $E = 44.4$ to 287.6 kJ mol^{-1} or preferentially from 82 to 150 kJ mol^{-1}. The reaction order n takes the values $0 \leq n \leq 2$, while the natural logarithm of the frequency constant ranges from $\ln(A/\text{min}^{-1}) = 4$ to 38. The authors [27–34] give different values of the estimated kinetic parameters for reaction (17). No uniform opinion concerning this fluctuation has been presented: the influence of the measurement conditions and the mathematical formalism assumed have been indicated as the main reasons.

The relatively complicated progress of reaction (17) (despite the simple notation of its equation) resulting from a change in the reaction mechanism, has also been indicated as a cause of the variations [34]. It has been assumed that initially the reaction runs according to the F1 mechanism ($n = 1, m = p = 0$), later changing to the R2 mechanism ($n = 1/2, m = p = 0$) [34].

2. Experimental

Commercial calcium oxalate monohydrate was used without further purification. Thermogravimetric analyses were performed in three different TG units: MOM OD-103 derivatograph; TG–DTA Setaram TAG 24 thermoanalyser; Mettler TA4000 thermobalance.

All runs were carried out in open platinum crucibles under inert atmosphere (argon, 200 cm^3 min^{-1}). The temperature increase rate was 10 K min^{-1}, and the sample weights were 50, 43.3 and 30.838 mg.

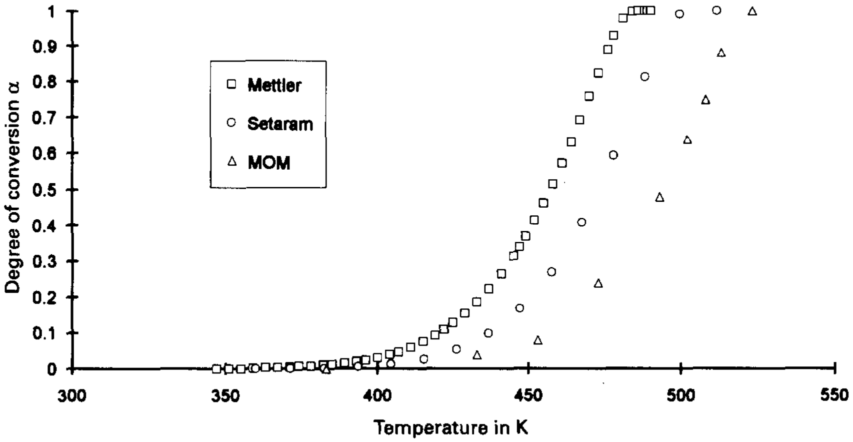

Fig. 2. The temperature range of $CaC_2O_4 \cdot H_2O$ dehydration observed on different measurement apparatus.

3. Results and discussion

The temperature range in which the weight changes were observed depended upon the measurement apparatus (Fig. 2): 110–250°C for the MOM; 86.8–238.6°C for the Setaram; and 74–217°C for the Mettler.

The kinetic parameters estimated for the dehydration of $CaC_2O_4 \cdot H_2O$ are shown in Tables 2a–c. It appears from Fig. 3, which shows data for series I from Table 2a, that the experimental data are practically consistent with those calculated for $0 < \alpha \lesssim 0.72$. The essential differences in the function course can be observed

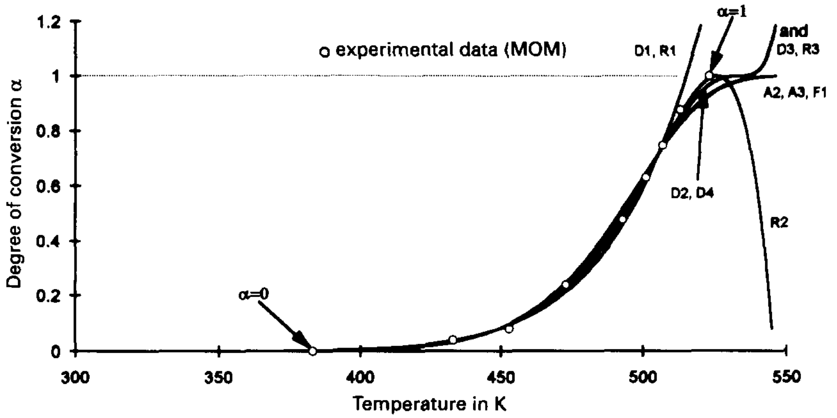

Fig. 3. Dependence of the conversion degree on absolute temperature for the individual assumed reaction mechanisms of $CaC_2O_4 \cdot H_2O$ dehydration.

Table 2
Kinetic parameters for dehydration of calcium oxalate monohydrate

Mechanism label	E/(kJ mol^{-1})	ln(A/min^{-1})	r	r^2/%
(a) MOM OD-103 derivatograph				
Series I ($N = 7$)				
F1	83.47	19.17	−0.994	98.80
R1	66.06	14.22	−0.997	99.33
R2	74.07	16.51	−0.997	99.42
R3	77.05	17.35	−0.997	99.30
A2	37.82	7.39	−0.993	98.59
A3	22.60	3.22	−0.992	98.30
D1	139.97	31.54	−0.997	99.40
D2	149.86	34.29	−0.998	99.51
D3	161.93	36.54	−0.997	99.35
D4	153.84	34.30	−0.998	99.49
(b) Setaram thermoanalyser				
Series II ($N = 13$)				
F1	87.01	21.14	−0.995	98.91
R1	75.37	17.50	−0.993	98.67
R2	80.03	19.05	−0.997	99.29
R3	82.30	19.67	−0.997	99.34
A2	39.94	8.50	−0.994	98.76
A3	24.24	4.05	−0.993	98.56
D1	157.87	37.77	−0.994	98.80
D2	163.66	39.55	−0.996	99.19
D3	171.75	40.92	−0.997	99.38
D4	166.25	39.24	−0.997	99.31
(c) Mettler thermobalance				
Series IIIa ($N = 18$)				
F1	79.83	20.12	−0.996	99.10
R1	67.64	16.08	−0.995	98.90
R2	72.72	14.77	−0.998	99.54
R3	74.83	15.07	−0.998	99.56
A2	36.48	7.98	−0.995	98.96
A3	22.03	3.69	−0.994	98.76
D1	142.15	35.65	−0.995	99.04
D2	148.04	36.88	−0.997	99.44
D3	156.52	38.13	−0.998	99.60
D4	150.75	36.25	−0.998	99.54
Series IIIb ($N = 142$)				
F1	79.7	20.03	−0.994	98.78
R1	68.55	16.37	−0.992	98.41
R2	73.09	17.18	−0.996	99.21
R3	75.01	17.40	−0.997	99.30
A2	36.43	7.94	−0.993	98.57
A3	22.00	3.67	−0.991	98.30
D1	143.94	36.22	−0.993	98.59
D2	149.21	37.23	−0.995	99.07
D3	156.87	38.18	−0.997	99.36
D4	151.62	36.50	−0.996	99.22

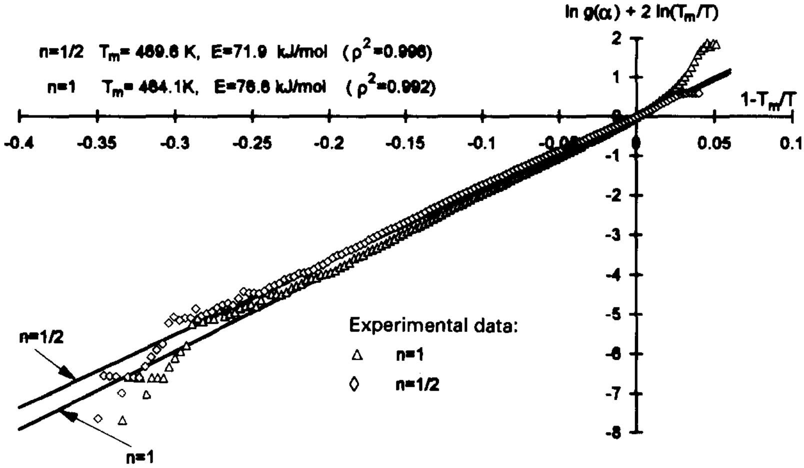

Fig. 4. Kinetic analysis of the conversion degree of $CaC_2O_4 \cdot H_2O$ dehydration for $n = 1/2$ and $n = 1$ (Mettler thermobalance).

above the upper inequality limit and inside the physical non-sense range, i.e. for $\alpha > 1$. From Tables 2a–c and Fig. 3, no rules can be concluded concerning the choice of a proper mechanism which could distinctly differentiate a particular reaction. An increase in the measurement points ($N = 7 \rightarrow 142$) to enhance the accuracy of the measurements results in obliterating the difference between the F1 and R2 mechanisms which were suggested in Ref. [34].

Incorporating the supplementary parameter T_m, using Eq. (4), suggests that the R2 mechanism ($n = 1/2$) is preferable to F1 ($n = 1$), as can be seen in Fig. 4.

The estimated values of the kinetic constants ln A and E meet the isokinetic effect of all cases, which means that the activation energy for the reaction of $CaC_2O_4 \cdot H_2O$ dehydration lies in the range $E = 30–180$ kJ mol^{-1}. The selection of the mechanism becomes even more complicated when the remaining mechanisms, i.e. those not included in Tables 2a–c, are incorporated into the analysis. Thus for the diffusion mechanisms, functions D1–D4, the activation energy takes very high values. This is inconsistent with the actual values reported for diffusion processes [35].

The results shown in Tables 2a–c can be combined with the isokinetic effect analysis according to Eqs. (15) and (16):

For series I: $\ln A = -1.308 + 0.235E$ ($r^2 = 99.82\%$). T_m from the DTG curve equals 523 K; calculated T_m equals 510.8 K.

For series II: $\ln A = -1.121 + 0.247E$ ($r^2 = 99.86\%$). T_m from the DTG curve equals 488.25 K; calculated T_m equals 487.7 K.

For series IIIa: $\ln A = -1.107 + 0.255E$ ($r^2 = 99.83\%$). T_m from the DTG curve equals 471 K; calculated T_m equals 472.2 K.

For series IIIb: $\ln A = -1.133 + 0.255E$ ($r^2 = 99.84\%$). T_m from the DTG curve equals 471 K; calculated T_m equals 471.6 K.

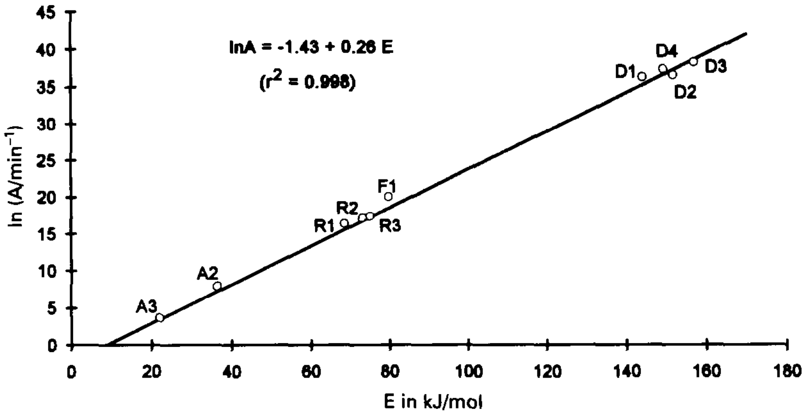

Fig. 5. Isokinetic effect from the assumption of different mechanisms for the $CaC_2O_4 \cdot H_2O$ dehydration.

Fig. 5 shows the example from series IIIb which provided the largest number of experimental data. The agreement of the experimental temperature, i.e. that determined from the weight loss DTG curve, with that calculated from Eq. (16) increases with increasing accuracy of thermogravimetric analyses performed (series II and IIIb). It should be mentioned, however, that this agreement could also derive from the apparatus sensitivity, i.e. the accuracy of the measurement of the temperature for the maximal reaction rate during the experiment.

The analyses performed lead to the conclusion that the reaction mechanism symbolised in Eq. (1) by $f(\alpha)$, involving its modifications, can result in an infinite number of statistically proper kinetic parameters which show the isokinetic effect. It still lacks, however, the unambiguous criterion that would allow reaction (17) to be used to determine the specific value of the activation energy.

4. The temperature criterion

Szarawara and co-workers [36–38], analysing the linear function (18), have introduced the temperature criterion

$$\ln \alpha = -\frac{E}{RT} + \text{constant} \qquad 0 < \alpha \lesssim 0.2 \tag{18}$$

to estimate the approximated activation energy of the processes proceeding in the kinetic range noted.

The connection of the temperature criterion (18) with the general kinetic equation for the non-isothermal condition (1) can be proved. After variable separation in Eq. (1), the following assumptions are made. On the left side of the equation, kinetics of zero order is introduced (the R1 mechanism); the $f(\alpha) = 1$ or $g(\alpha)$ function is expanded into a series for the F1, Fn, and R2–R3 mechanisms, while the series expansion is limited to the first term, i.e. $g(\alpha) \cong \alpha$. On the right side of the equation, the rounded Doyle's approximation for the integral solution is assumed [1]

$$\frac{A}{q}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \cong C\frac{AE}{qR}\exp\left(-\frac{E}{RT}\right) \tag{19}$$

where C is close to 0.005.

Thus we obtain as a result

$$\alpha = \frac{CAE}{qR}\,\mathrm{e}^{-E/RT} = \text{constant}\ \mathrm{e}^{-E/RT} \qquad 0 < \alpha \lesssim 0.2 \tag{20}$$

On the basis of the above analysis, criterion (18) raises a supplementary possibility that the activation energy can be estimated, which would eliminate the necessity of

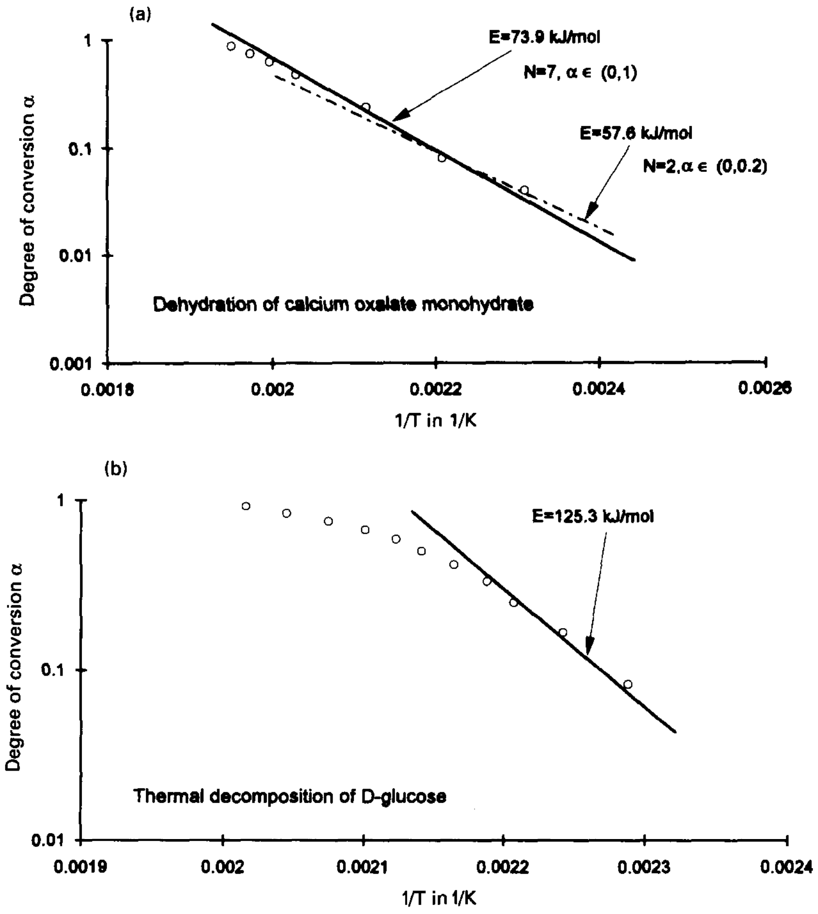

Fig. 6. Activation energy approximated for: (a) $CaC_2O_4 \cdot H_2O$ dehydration process and (b) D-glucose thermal decomposition, as derived from the temperature criterion, Eq. (18).

introducing the $g(\alpha)$ function displaying the process mechanism and the solution of temperature integral. Thus interpretation of Eq. (18) can be extended. Practical use of criterion (18) to estimate the activation energy for the TG measurements of reaction (17) of series I is shown in Fig. 6a. Fig. 6b illustrates a similar analysis for the thermal decomposition of D-glucose on the basis of the data extracted from Tanaka's studies (reference 11 in Ref. [1]).

The activation energy values estimated are consistent with the data obtained by using the $f(\alpha)$ function, which characterizes the reaction mechanism. It can be concluded that the activation energy estimated from criterion (18) univocally determines the most probable mechanism which comes from the $f(\alpha)$ form. This may not always be true for more complicated examples.

5. Analysis of more complicated examples

One of the systematic errors in the interpretation of kinetic data on the basis of thermogravimetric analyses comes from the unthinking application of the theoretically possible kinetic models to the experimental measurements. Selective choice of the data can also be observed, as for example, in series IIIa where the edge values for $\alpha \to 0$ or 1 are excluded. At the same time the statistical correlative tests of r^2, ρ^2 are maximized $\to 1$. The above-mentioned procedures often result in the elimination of important information and the overlooking of interesting phenomena that derive from thermogravimetric analyses under dynamic conditions.

Thus a kinetic interpretation of the experimental data should disregard assumed models which can have no logical basis. The models that are statistically more significant, and result in explanation and interpretation of the process being analysed should also be taken into account and verified. Below we show three examples that are more complicated than reaction (17) and Fig. 6.

5.1. Example 1: Change in the activation energy

The example shows the analysis performed using the data published by Khadikar et al. (Tables 3 and 4 in Ref. [39]). The authors studied the mass loss for the copper(II) chelate of salicylhydrazide shown schematically as

$$Cu^{2+}(sh)_2 \cdot 2H_2O(s) \to Cu^{2+}(sh)_2(s) + 2H_2O(g) \qquad (21)$$

where sh is salicylhydrazide. The average kinetic parameters evaluated by the authors were $E = 65.78$ kJ mol^{-1} and $\ln(A/\text{min}^{-1}) = 17.44$.

It can be seen in Fig. 7 that using solution (3) results in the measurement data falling along two straight lines. This suggests a two-stage process for reaction (21). The activation energies are 26.73 and 71.25 kJ mol^{-1}, respectively. The temperature criterion (Fig. 8) gives the value $E = 32.9$ kJ mol^{-1} which is closer to that of the first step shown in Fig. 7.

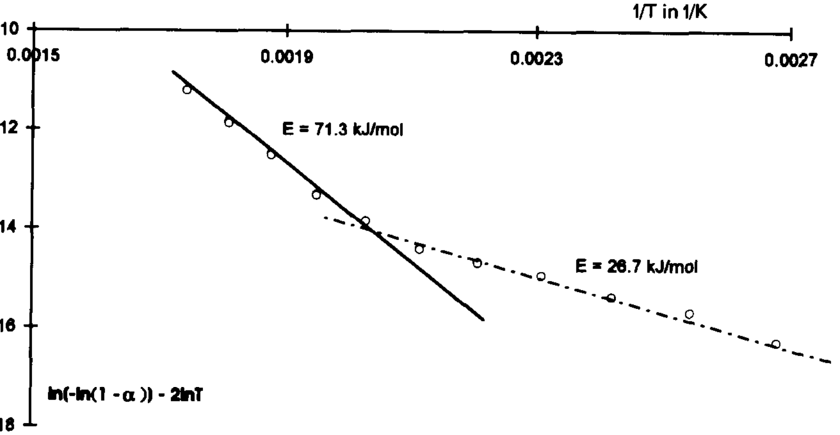

Fig. 7. Kinetic interpretation of the dehydration of the copper(II) chelate of salicylhydrazide, assuming first-order kinetics, i.e. the F1 mechanism, and solution (3).

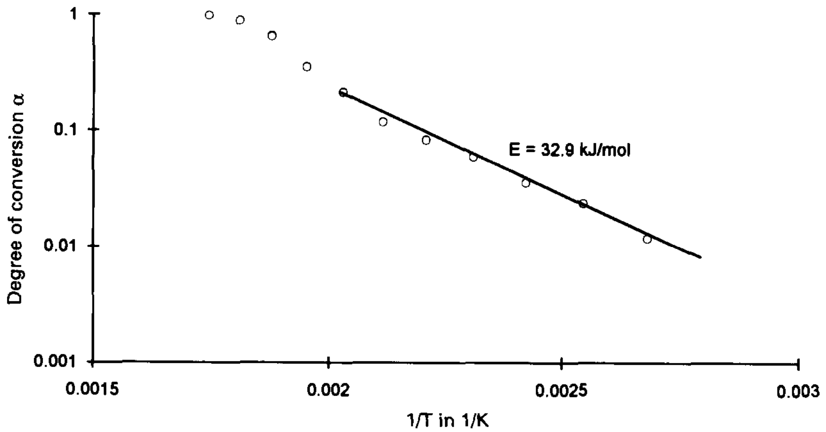

Fig. 8. Activation energy approximated for the copper(II) chelate of salicylhydrazide, from the temperature criterion, Eq. (18).

This analysis proves that combined testing of models (3) and (18) (Figs. 7 and 8) enriches the description of the chemical reaction progress. It can be concluded that the first stage probably involves the smooth removal of the one water molecule, with an activation energy of ≈ 30 kJ mol^{-1}.

5.2. Example 2: Thermal stability of high molecular-weight compounds (polymers)

The conservation of the standardizing conditions for transformation from definition (13) to (14) poses problems for complex substances including polymers, because a knowledge of the polymer molecular weight is necessary for this operation. The reaction order obtained from relation (8) or (9) (assuming that the progress of the process can be displayed by Eq. (1) and E = idem) is also of vital importance. Despite reservations concerning the solution of the kinetics, use of Eq. (1) in the form of Eq. (4) is recommended.

Data for this example were extracted from Adam et al. [40] (Table 1) for the decomposition of PVC (Sicron 548) accompanied by evolution of hydrogen chloride. The temperature of the maximal decomposition rate of PVC estimated from DTG is $T_m = 538$ K [40]. From this, the absurd reaction order of $n = 27$ and an energy of activation of $E = 2080$ kJ mol^{-1} are obtained. However, graphical differentiation of the conversion degree versus temperature curve gives a reaction order of $n = 3$ as the most probable value. Fig. 9a illustrates the kinetics of the reaction analysed for the different reaction orders assumed. For the activation energies and frequency constants estimated, the parameters for the isokinetic effect

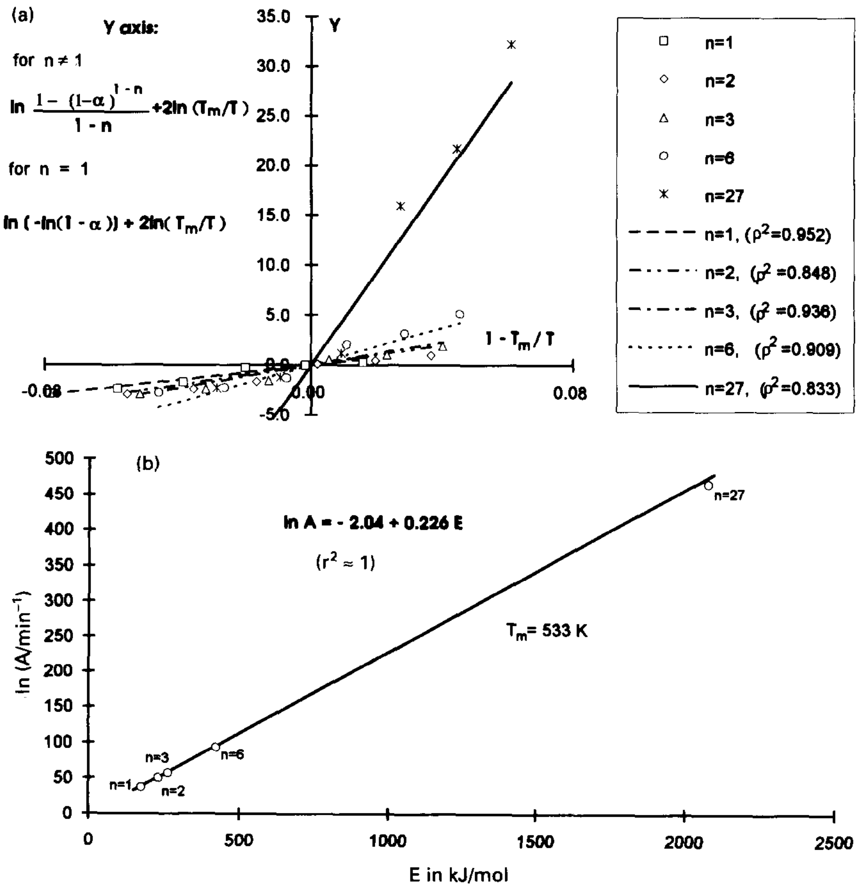

Fig. 9. Thermal decomposition of PVC: (a) kinetic analysis for solution (4) and different reaction orders ($n = 1, 2, 3, 6, 27$); (b) isokinetic effect derived from the assumption of the different values of n.

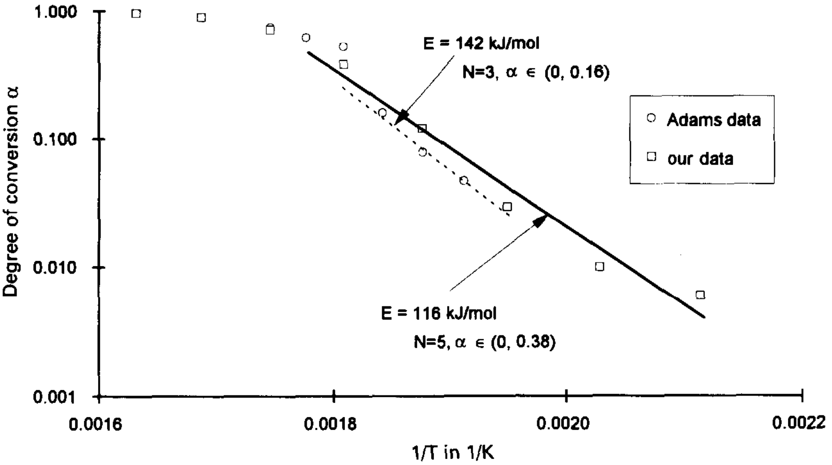

Fig. 10. Activation energy for PCV decomposition approximated on the basis of the temperature criterion, Eq. (18): data of Adam et al. [40] and our data.

are determined. On the basis of this effect, T_m is 533 K which is closest to the maximal temperature of the reaction version of $n = 27$, which we have just rejected. So the isokinetic effect (Fig. 9b) does not decide between the models' correctness or likelihood.

The activation energy $E = 142.0\ \mathrm{kJ\ mol^{-1}}$ estimated from the temperature criterion (Fig. 10) is, however, closer to the values found in the literature [41], i.e. $E = 125\ \mathrm{kJ\ mol^{-1}}$.

It has been established from the PVC thermal decomposition studied in our laboratory (Derivatograph MOM OD-103) that the process mechanism is best described by the F*n* ($n = 1.6$) mechanism. The activation energy estimated assuming this mechanism amounts to 130.7 kJ $\mathrm{mol^{-1}}$. Thus, it seems that the temperature criterion enables the most probable activation energy to be determined for the data extracted from Ref. [40].

5.3. Example 3: Analysis of the thermal conversions of hard coals

Very few applications of Eq. (1) to the analysis of coal pyrolysis have been found in the literature: apart from Ref. [3], some other studies have been mentioned in Ref. [2]. This is because there are difficulties with defining and setting many of the basic initial parameters which are essential to the construction of the appropriate mathematical model describing the pyrolysis process. The method for analysing the thermal decomposition of coals based on the different kinetic models F1 and F*n* has been presented in Ref. [42]. Specific kinetic characteristics suggest that the pyrolysis of dry hard coal can be divided into two stages.

The first stage involves physicochemical processes connected with the foundation and hardening of coke structure which is typical of coals. The second includes

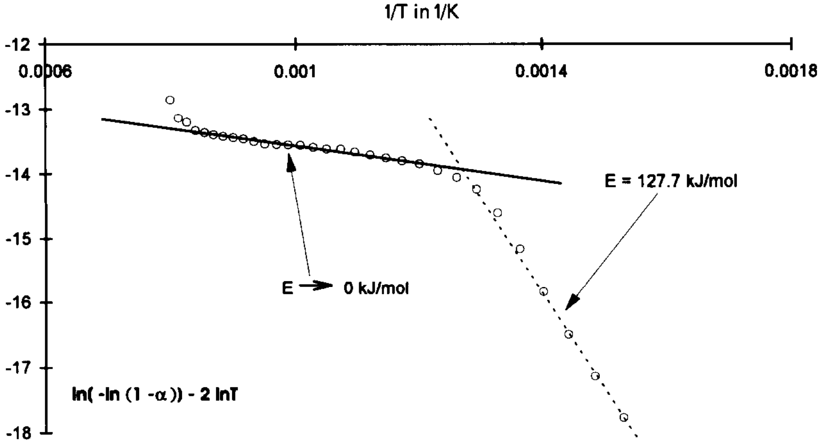

Fig. 11. Kinetic analysis for coal pyrolysis (gross process), assuming first-order kinetics and solution (3).

secondary coke carbonization at 1073 K. The kinetic characteristics for the "gross process" (Fig. 11) seem to show that in the range of the first pyrolysis stage, a change in the activation energy takes place. Near the end of this stage, its value tends to zero. Therefore, it is assumed that in the first stage of coal pyrolysis the process transforms from the fast kinetic range into a diffusion regime. To describe this stage, two types of equation are proposed [42].

(i) For processes in the kinetic range, first-order kinetics (F1) is assumed; according to supplementary conditions shown in Ref. [2], the final equation is obtained in the form

$$-\ln(1-\alpha_K) = \frac{A_K R T^2}{qE}\, e^{-E/RT} \tag{22}$$

(ii) For the processes in the diffusion range, first-order kinetics is assumed; provided (Fig. 11) that $E \cong 0$, Eq. (1) takes the form

$$-\ln(1-\alpha_D) = \frac{A_D}{q}\,\Delta T \qquad \Delta T = T - T_D \tag{23}$$

Fig. 12 analyses an example of coal (type 534, according to international classification) extracted from Ref. [42]. Thus the dependencies of the conversion degrees α_K and α_D as described by Eqs. (22) and (23) against temperature are presented. The activation energy estimated according to the temperature criterion ($E = 139$ kJ mol^{-1}) is close to the value of activation energy for the kinetic range of the first pyrolysis step estimated according to Eq. (20) ($E = 138.9$ kJ mol^{-1}). Thus complex analysis of thermogravimetric data for the thermal decomposition of coal provides a deeper understanding of the kinetic characteristics of the process analysed.

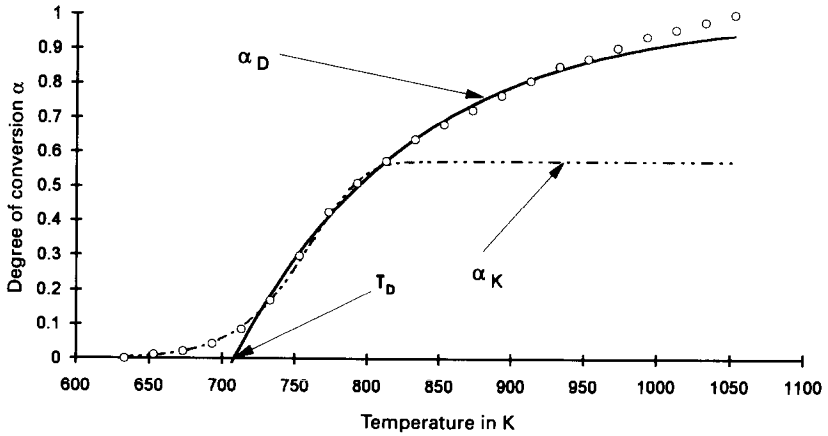

Fig. 12. The functions of α_K and α_D for the coal sample analysed in Fig. 11.

6. Conclusions

The kinetic interpretation of thermogravimetric characteristics based on Eq. (1) results in numerous estimation values of the kinetic parameters, i.e. the activation energy E and frequency constant A in the Arrhenius equation, that depend on the assumed process mechanism represented by the $f(\alpha)$ function. The isokinetic effect has been found for examples characterized by good correlation for different mechanisms according to Eq. (3). The maximal reaction rate temperature according to Eq. (16) or, more strictly, the dimensionless activation energy E/RT_m occurs in the effect. Although the isokinetic effect may form a test verifying the correctness of the form of the assumed equation for the process analysed, it does not unequivocally indicate the process kinetics.

A temperature criterion, Eq. (18), to verify and determine the most probable reaction mechanism has been proposed. It enables estimation of the activation energy for low conversion degrees. For more complicated examples, analysis should be performed on the appropriate basis of experimental data and complex thermogravimetric characteristics.

Analysis of the solution of Eq. (1) in both forms of Eqs. (3) and (4), and the isokinetic effect, Eqs. (15) and (16), enriches the thermokinetic characteristics of the process with new forms derived from additional assumptions in Eq. (1), as can be illustrated by Eqs. (22) and (23).

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