

THE KISSINGER LAW AND ISOKINETIC EFFECT Part I. Most common solutions of thermokinetic equations

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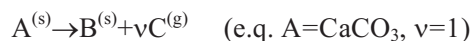
Abstract

We performed the analysis of the thermokinetic equations taking into account Kissinger law. The formulas obtained were verified by the use of the so-called isokinetic effect. It was shown that the thermokinetic equation, $g(\alpha) = (AT/q)\exp(-E/RT)$, appeared to connect both laws analyzed. Moreover, this approach validates equation $k_m = q/T_m$ which takes a form of Kissinger law, i.e. $\ln(q/T_m)$ vs. $1/T_m$.

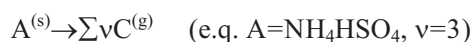
Keywords: isokinetic/compensation effect, Kissinger law, thermokinetic equations

Introduction and the aim of the work

We consider thermal decomposition of chemically defined compounds



or



(1)

The aim of current publication is analyze the relation between thermokinetic Eqs (17) and (18) which can both take a form of the well-known formulas given by Kissinger law or the so-called compensation effect which is also known as isokinetic effect [1, 2].

Therefore, we have two different thermokinetic equations describing dynamic conditions ($q > 0$). In fact, no criteria are known which would provide any information which of the equations is the proper one and which one is only the approximation.

Isothermal and isobaric conditions

The kinetic equation for isothermal conditions ($T = \text{constant}$) is usually given by the relationship between the conversion degree ($0 \leq \alpha \leq 1$) and the time (τ), it's necessary restriction $T > T_{\text{eq}}$

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$$\frac{d\alpha}{d\tau} = k(T)f(\alpha) \quad (2)$$

or the integral form

$$g(\alpha) = k(T)\tau, \text{ where } g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad (3)$$

In the isothermal (and isobaric) conditions we make use of the Arrhenius law which is usually noted in its classical form $k(T) = A \exp(-E/RT)$.

If reaction runs in temperature $T < T_{\text{eq}}$ (reversible reaction) then initial Eq. (2) should be in form, which assure that the end of reaction would take place after acceding to the equilibrium conversion degree (α_{eq}) after some time, what does not mean that reacting (total thermal decomposition) of compound A [3] has taken place and, in this context, we write Eq. (2) in form as following [4–8]:

$$\frac{d\alpha}{d\tau} = k(T)f(\alpha)[1 - e^{-\Delta G/RT}], T = \text{const.} \quad (4)$$

One can prove that (we omit the proof):

$$\Delta G = -vRT \ln(\alpha/\alpha_{\text{eq}}) \quad (5)$$

For thermal decomposition of A compound (1) Eq. (4) may be presented as following:

$$\frac{d\alpha}{d\tau} = k(T)f(\alpha) \left[1 - \left(\frac{\alpha}{\alpha_{\text{eq}}} \right)^v \right] \quad (6)$$

where $\eta = \alpha/\alpha_{\text{eq}}$ is the thermodynamic yield of reaction [9] and α_{eq} is only a function of temperature T . Consequently,

$$\frac{d\alpha_{\text{eq}}}{d\tau} = 0 \quad (7)$$

From Eq. (6) follow two facts:

(i) process takes place 'very far' from equilibrium [7], $\alpha \ll \alpha_{\text{eq}}$, transformation of Eq. (6) to Eq. (2),

(ii) when $\alpha = \alpha_{\text{eq}}$ then $d\alpha/d\tau = 0$ (8)

This signifies the end of reaction, which in a given temperature reaches at most the value of the conversion degree equal to α_{eq} . According to modified van't Hoff's equation in the form [9]

$$\ln \alpha_{\text{eq}} = -\frac{\Delta H_d}{vR} \left(\frac{1}{T} - \frac{1}{T_{\text{eq}}} \right) \quad (9)$$

when $T = T_{\text{eq}}$ then $\alpha_{\text{eq}} = 1$.

Let Fig. 1 (data have been taken from [10]) illustrate how the mentioned problems are important in research works investigating in particular the heterophase processes of type (1). The maximal conversion degree has been acceded ($A=CaCO_3$) for $\alpha=0.1605$, $\alpha_{eq}=0.6517$ ($T=1123$ K). The results of quoted researches have been already analyzed in our previous works [9, 11].

Figure 1 is an illustration of assumption (i), or profiting from form (2), taken for isothermal conditions.

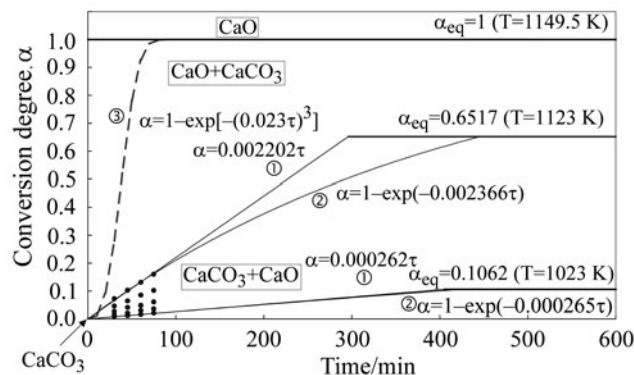


Fig. 1 Relation between conversion degree vs. time in isothermal conditions, $CaCO_3 \leftrightarrow CaO + CO_2$. 1) $\alpha = k(T)\tau$, kinetic of 0-order; 2) $\alpha = 1 - \exp[-k(T)\tau]$, kinetic of Ith order; 3) probably path; 4) • experimental data (from [10]), $\ln \alpha_{eq} = -173317.8/\nu RT + 18.135$, $\nu = 1$, $T_{eq} = 1149.5$ K (from [9])

Actually, thermal decomposition of $CaCO_3$ is a complex process. This complexity can be illustrated by the following:

- polymorphic changes appear, for example: calcite–vaterite [12],
- mechanism of decomposition by Jovanovic (loc. cit. [12]) assumes existing metastable $CaCO_3$ and CaO ,
- $CaCO_3$ and CaO can form eutectics and/or solutions.

Nevertheless, $CaCO_3$ is used as a model compound for thermokinetic considerations (Conference ICTAC, USA, 1996, [13–17] especially part B [14]).

Introduction to dynamic equations

The problem gets complicated, however, if we shift to dynamic conditions. Thus, we most often observe the linear temperature increase, which is given by:

$$q = dT/d\tau \text{ or } T = T_i + q\tau, q > 0, T_i = 0 \text{ K} \tag{10}$$

and consequently

$$q = T/\tau, \tau > 0 \tag{11}$$

The intercept in Eq. (10) may be equal to 0 [4, 5, 7] and may express the initial temperature (e.g. $T_i=298$ K [3]) or equilibrium temperature of conversion [6, 8]. As published by Vyazovkin and Wight in [18], in the case of the constant heating rate (10) we can make the trivial transformation to the form:

$$\frac{d\alpha}{dT} = \frac{1}{q} \frac{d\alpha}{d\tau} \quad (12)$$

Formula (12) is typical, e.g. in paper [13–17], and is correct from mathematical point of view only.

We accept van't Hoff's modification (9) and we differentiate

$$\frac{d\alpha_{eq}}{dT} = \alpha_{eq} \frac{\Delta H_d}{vRT^2} \quad (13)$$

when $\alpha=\alpha_{eq}$ (assumption):

$$\frac{d\alpha}{dT} = \alpha \frac{vR}{\Delta H_d} \left(\frac{\Delta H_d}{vRT_{eq}} - \ln\alpha \right)^2 \quad (14)$$

We attribute $\alpha=1$ to the end of reaction temperature T_{eq} (complete decomposition of compound A). Then in accordance with Eq. (13)

$$\left(\frac{d\alpha}{dT} \right)_{T=T_{eq}} = \frac{\Delta H_d}{vRT_{eq}^2} \neq 0 \quad \text{while} \quad \left(\frac{d\alpha}{d\tau} \right)_{T \geq T_{eq}} = 0 \quad (15)$$

Consequently, in temperature T_{eq} we have

$$\frac{d\alpha}{d\tau} = 0 \quad \text{and} \quad 0 \leq \frac{d\alpha}{dT} \leq \frac{\Delta H_d}{vRT_{eq}^2} \quad \left(\text{straight line parallel to } \frac{d\alpha}{dT} \right) \quad (16)$$

For condition $(d^2\alpha/dT^2)=0$ from Eq. (13) we obtain $T_m = \Delta H_d/2vR$. It means, that $T_m \gg T_{eq}$.

To some extent formula (16) opposes Eq. (12). Moreover, it suggests that the rate constant of the chemical process can definitely given by $(d\alpha/d\tau)$ even in the dynamic conditions. This is a fundamental principle of Šesták's *et al.* approach [6, 8, 19–23]. The main problem is however that Eq. (12) meets universal acceptance, being a kind of bridge linking kinetic equations for isothermal conditions with the dynamic ones in a case of linear temperature increase.

Dynamic conditions

We show below the so-called thermokinetic equation that results from a well-known modification of Eq. (2) that includes Eq. (12), classical Arrhenius law and the differential formula giving the heating rate (q).

$$\frac{d\alpha}{dT} = \frac{A}{q} e^{-E/RT} f(\alpha), \quad q > 0 \quad (17)$$

However, if we analyze the equation for the total differential defining the increase of the conversion degree (α), then according to previous publications [4, 5, 24] we obtain the thermokinetic equation in a form of

$$\frac{d\alpha}{dT} = \frac{A}{q} e^{-E/RT} f(\alpha) \left(1 + \frac{E}{RT} \right), \quad q > 0 \quad (18)$$

Interrelations between (E) and (RT) were discussed in a number of publications, e.g., [24–28]. In the current work we used Eqs (17) and (18) as a starting point for further analysis.

By experience, we know that in dynamic conditions the total thermal decomposition of compound A to B (or to the sum of gaseous product C) must always occur, so $\alpha = \alpha_{\text{eq}} = 1$. Then Eq. (12) should be introduced into Eq. (6) and, expressed by $d\alpha/dT$, may be solved by way of numeric calculations. Degree of complication of this problem has caused boundless reliance in Eq. (17).

An affair, resulting from assumptions for whose Eq. (18) has been formed, is also complicated.

In historical approach MacCallum and Tanner [29] have proposed the differential equation for dynamic conditions, as following:

$$\frac{d\alpha}{d\tau} = \left(\frac{\partial \alpha}{\partial \tau} \right)_{\tau} + \left(\frac{\partial \alpha}{\partial T} \right)_{\tau} q \quad (19)$$

or alternatively [5]:

$$\frac{d\alpha}{dT} = \left(\frac{\partial \alpha}{\partial \tau} \right)_{\tau} \frac{1}{q} + \left(\frac{\partial \alpha}{\partial T} \right)_{\tau} \quad (20)$$

Mentioned complexity of problem results from the fact that, starting from the date of publication in 1970 [29], the heated discussions connected with existence of partial derivative [4, 5, 7] or with lack of $(\partial \alpha / \partial T)_{\tau}$ its physical sense have flared up [6, 8, 19]. It is necessary to take for isothermal and dynamic process the following equation, after all:

$$\frac{d\alpha}{d\tau} = \left(\frac{\partial \alpha}{\partial \tau} \right)_{\tau} = \left(\frac{\partial \alpha}{\partial \tau} \right)_{\text{q}} \quad (21)$$

It means that Eq. (18) derived by way of considerations given in [4, 5, 24] is subjected to discussion. Let us observe, when we introduce ratio (11) $T_i = 0$ K, directly into Eq. (3) and when we take the conventional $k(T)$ equation then, after differentiating with regard to temperature, we obtain the form (18).

The present work does not take on further possibilities of using of discussed establishments (6), (19) or (20), admitting that Eqs (17) and (18), with tacit agreement

as to their correctness, are used adequately in great number of research works. However, in most of the works definitely, one uses Eq. (17).

The conversion degree (α) is understood as a ratio of amount of reacted moles of A compound to its initial amount of moles, so that as well for isothermal conditions as for dynamic ones the relations arrive, as following (compare [8] or [21])

$$0 \leq \alpha \leq \alpha_{\text{eq}}, \quad 0 < \alpha_{\text{eq}} \leq 1 \quad (22)$$

Analysis of the problem

A/ The Kissinger law

Usually the solutions of differential Eq. (17) are to take a form [30]:

$$g(\alpha) = \frac{ART^2}{qE} e^{-E/RT} \quad (23)$$

$$g(\alpha) = \frac{AT}{q} e^{-E/RT} \quad (24)$$

$$g(\alpha) = 0.00484 \frac{AE}{qR} e^{-1.0516E/RT}, \quad 20 < \frac{E}{RT} < 60 \quad (25)$$

(Doyle's approximation)

The solutions that are different than those given by Eqs (23–25) are discussed in many publications [6, 30–35]. In this context, both the number of possible solutions as well as the controversies over a form of these solutions [36] is the main issue.

We start from the Kissinger law that comes from the condition (26)

$$\frac{d^2\alpha}{dT^2} = 0, \quad T = T_m \quad (26)$$

and from Eq. (23) we obtain

$$\frac{E}{RT_m^2} - \delta \frac{A}{q} e^{-E/RT_m} = 0 \quad (27)$$

in which we evaluate

$$\delta = - \frac{df(\alpha_m)}{d\alpha_m} \quad (28)$$

which is a specific form of a function (compare [22, 37]):

$$h(\alpha) = - \frac{df(\alpha)}{d\alpha} \quad (29)$$

We analyzed conditions (26) and (27) using Eq. (17), however with the proviso that the $f(\alpha)$ function is limited to the n^{th} ($n > 0$) order kinetics and does not refer to 0^{th} order mechanism. For the $f(\alpha)$ functions of the F_n ($n > 1$), R2, R3 and A2, A3 symbols we obtain (Table 1):

$$\delta = 1 \tag{30}$$

Table 1 The analysis of the conditions (37) and (28) for the known $f(\alpha)$ and $g(\alpha)$ models

Mechanism label	For which α_m (condition (37))	The δ value for the condition (28)
F1	$\alpha_m = 1 - e^{-1} = 0.632$	$0 \leq \alpha \leq 1, \delta = 1$
$F_n, n > 1$	$\alpha_m = 1 - n^{(1-n)-1}$	$0 \leq \alpha \leq 1, \delta = 1$
R1	$\alpha_m = 1$	$\delta = 0$ (never)
R2	$\alpha_m = 3/4 = 0.75$	$\delta = 1$
R3	$\alpha_m = 1 - (2/3)^3 = 0.704$	$\delta = 1$
A1	$\alpha_m = e(1+e)^{-1} = 0.731$	$\delta = \frac{e-1}{e+1} = 0.46$ (never)
A2	$\alpha_m = 1 - e^{-1} = 0.632$	$\delta = 1$
A3	$\alpha_m = 1 - e^{-1} = 0.632$	$\delta = 1$
2F1-R1*	$2\ln(1-\alpha_m) + \alpha_m + 1 = 0$ $\alpha_m \cong 0.536$	$\delta \cong -0.651, (0 \leq \alpha \leq 1, 0 \leq \delta \leq 1/2)$
D1, $g(\alpha) = \alpha^2/2$	$0 \leq g(\alpha) \leq 1/2$	$\alpha_m > 1$ $(\delta = 1/2, \alpha_m = \sqrt{2})$
D1', $g(\alpha) = \alpha^2$	$\alpha_m = 1$	$\delta = 1, \alpha_m = \sqrt{2}/2$
D2	$\alpha_m \rightarrow 1$	$1 < \delta < \infty$ $\delta \rightarrow \infty$ (never) $(\delta_{\min} = e^2/4 = 1.847,$ $\alpha = 1 - e^{-2} = 0.8647)$
D3**	$\alpha_m = 1 - (1 - \sqrt{2/3})^3 = 0.9938$	$1 < \delta < \infty$ $\delta \cong 4.949$ (never) $\delta_{\min} = 3.697,$ $\alpha = 1 - [(3 - \sqrt{5})/2]^3 = 0.9443)$
D4**	$0 \leq g(\alpha) \leq 1/2$	$1 < \delta < \infty$ (never) $(\delta_{\min} = 5.333, \alpha = 1 - 0.5^3 = 0.875)$

* $f(\alpha) = (1-\alpha)(1+\alpha)^{-1}$

**the $g(\alpha)$ functions include the 3/2 coefficient

If we take the Kissinger law in a form of (27) with the proviso given by (30) and replace a term

$$\frac{A}{q} = \frac{E}{RT_m^2} e^{E/RT_m} \tag{31}$$

in Eqs (23) to (25) we obtain:

$$\text{from (23)} \quad g(\alpha) = \left(\frac{T}{T_m}\right)^2 \exp\left[\frac{E}{RT_m}\left(1 - \frac{T_m}{T}\right)\right] \quad (32)$$

$$\text{from (24)} \quad g(\alpha) = \left(\frac{T}{T_m}\right) \frac{E}{RT_m} \exp\left[\frac{E}{RT_m}\left(1 - \frac{T_m}{T}\right)\right] \quad (33)$$

$$\text{from (25)} \quad g(\alpha) \cong 0.005 \left(\frac{E}{RT_m}\right)^2 \exp\left[\frac{E}{RT_m}\left(1 - \frac{T_m}{T}\right)\right] \quad (34)$$

respectively.

It can be found that Eqs (32) to (34) which are solutions of the thermokinetic equation together with the Kissinger law (with proviso $\delta=1$) may take a linear form of:

$$\ln g(\alpha) + m \ln\left(\frac{T_m}{T}\right) = \ln C + \frac{E}{RT_m} \left(1 - \frac{T_m}{T}\right) \quad (35)$$

where $m=2, 1$ or 0 , $C=1, E/RT_m$ or $0.005(E/RT_m)^2$, respectively.

If $T=T_m$ (the temperature of the maximal reaction rate, condition (26)) only for $m=2$ and $C=1$ we obtain a condition

$$\ln g(\alpha_m) = 0 \quad (36)$$

Thus (e.g. from Eq. (32))

$$g(\alpha_m) = 1, T = T_m \quad (37)$$

At this point a controversy arouses if for all known mass integrals $g(\alpha)$:

- 1) derivative (28) fulfills the condition (30) and
- 2) condition (37) is always obeyed,

for the actual values taken by the conversion degree $0 \leq \alpha \leq 1$.

Table 1 shows the analysis performed in the reversed sequence. In fact, we need to know the conversion degree at the temperature of the maximal reaction rate α_m before we can calculate a specific value (28) for the derivative determined (29). The data shown in Table 1 indicate that for the F1 mechanisms (this case is quite obvious) and F_n ($n > 1$) and R2, R3, taking into account the modified first order kinetics, i.e., A2 and A3, we can observe that condition (30) is fulfilled, which means $\delta=1$ and simultaneously α_m can be found to take a value in the range of $0 < \alpha \leq 1$.

There is an α_m value that fulfills the condition mentioned above for the A1 models and the Dahme–Junker equation, which is a linear combination (2F1-R1), but the derivative $\delta \neq 1$. The diffusion models D1 to D4 describe more complicated cases. The D1 model in a form quite often found as $(g(\alpha) = \alpha^2/2)$ and D4 are limited by the values that can be taken by the mass integral $0 \leq g(\alpha) \leq 1/2$. However, if we assume other coefficients (that sound reasonable), e.g., $g(\alpha) = \alpha^2$, then the range analyzed changes, which makes possible $\alpha_m = 1$ and simultaneously $\delta = 1$. Although $\alpha^2 \rightarrow 1$ (or 0.994) for the D2 and D3 models, condition (30) can never be fulfilled. It is not sufficient to change the coefficients

for the D3 and D4 models, because the minimal values δ are always larger than 1. This indicates that it is very important to decide on the side of the function:

$$f(\alpha) \text{ or } g(\alpha)$$

to introduce numerical coefficients. Table 2 compares the approaches followed in [5, 38–47], indicating in particular the differences observed. This concerns the R2, R3, D1 and D3, D4 and sometimes F3 mechanisms.

Table 2 The $f(\alpha)$ and $g(\alpha)$ forms that can be found in the literature so frequently as these given in [2, 49]

Mechanism label	$f(\alpha)$	$g(\alpha)$	Ref.*
R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	[5, 38–47]
R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	[5, 38–47]
F3	$(1/2)(1-\alpha)^3$	$(1-\alpha)^{-2}$	[44–47]
D1	$(2\alpha)^{-1}$	α^2	[5, 39, 40, 42–47]
D3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$	[5, 39–47]
D4	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$	[5, 39–47]

*Differents acc. to [2, 49]

At this point it is not easy to decide on how to solve and normalize this problem. It can be speculated that the relationships of a form $f(\alpha)=(1-\alpha)^n$, where n is 0, 1, 2, 3 or a fraction, should be used generally. On the other hand, we can also assume the proper forms of the $g(\alpha)$ in such a form, as shown in Table 1.

The advantage of the latter solution is that allows the possibility to compare the R3 and D3 mechanisms in forms given by Table 1, which results in similar mathematical structures, e.g. $g(\alpha)=[1-(1-\alpha)^{1/3}]^p$, where $p=1$ (R3) or $p=2$ (D3) [48].

The analysis of function (29) for the diffusion models is shown in Fig. 2. It can be concluded from Fig. 1 and Table 1 that for the D2 to D4 models condition (30) can never be fulfilled. For the D1 model this can be achieved only by assuming a different

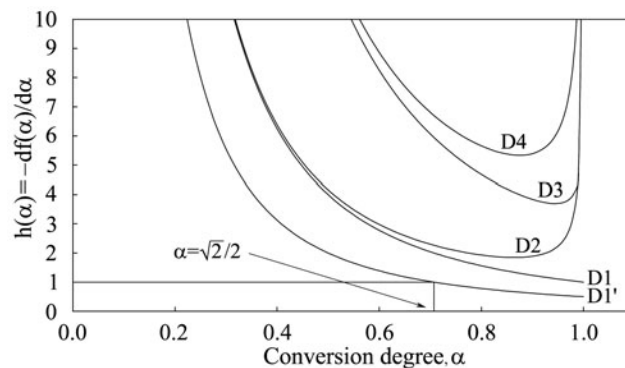


Fig. 2 The $h(\alpha)$ profile according to (29) – search for $\delta=1$

coefficient. Thus, theoretically for the D2 to D4 models also the condition (27) is not longer obeyed, because $\delta \gg 1$ and for the D2 and D3 models the maximal reaction rate is achieved just at the end of the thermal decay, similarly as for the modified D1 model ($\alpha_m=1$).

Therefore, it will be interesting to perform the analysis of such a case when the experimental data can be described by the diffusion model of the D type.

Analysis of the literature data

Table 3 analyzes the data published previously [49]. The initial data is given for the IIIb series ($N=142$ measurements).

Table 3 A fit of thermokinetic models and the averaged activation energy \bar{E} for the reaction of dehydration of calcium oxalate

Entry	Mechanism label	$E/\text{kJ mol}^{-1}$	b acc. to [9]	$\bar{E}/\text{kJ mol}^{-1}$ calculated ^b	$r^2/\%$	Remarks
1	D3	156.9	2	78.5	99.36	
2	R3	75.0	1	75.0	99.30	a) $r^2 > 99\%$
3	D4	151.6	2	75.8	99.22	b) $\bar{E} = E/b$
4	R2	73.1	1	73.1	99.21	c) $E = 71.9 - 76.6 \text{ kJ mol}^{-1}$
5	D2	149.2	2	74.6	99.07	[49], acc. to Eq. (32)
6	F1	79.7	1	79.1	98.78	rejected models
7	D1	143.9	2	72.0	98.59	
8	A2	36.4	1/2	72.8	98.57	
9	R1	68.6	1	68.6	98.41	
10	A3	22.0	1/3	66.0	98.30	
11	2F1-R1 ^d	84.9	1	84.9	98.29	
12	F2	100.6	1	100.6	87.68	
13	F3	126.4	1	126.4	73.17	

Significance level: 0.0⁽⁵⁾

The best-fitting thermokinetic models according to the determination coefficient $r^2(\%)$ are given in Table 3. The best model is the D3 one, followed by the R3, D4, R2 and D2, respectively. For the typical profile of the α vs. temperature (Fig. 3a) the reaction rate $d\alpha/dT$ vs. T reaches its maximum at the $T_m=471$ K (according to [49]). The corresponding conversion degree α_m takes a value lower than 1, moreover, this value is closer to the one given by the R2 model ($\alpha_m=0.75$) – Fig. 3b. Thus, we can conclude a substitution nature of the diffusion models and the models of the fraction type, which appeared from the fact that we can observe a clear deviation in the experimentally derived relationship of the conversion degrees vs. temperature in the final

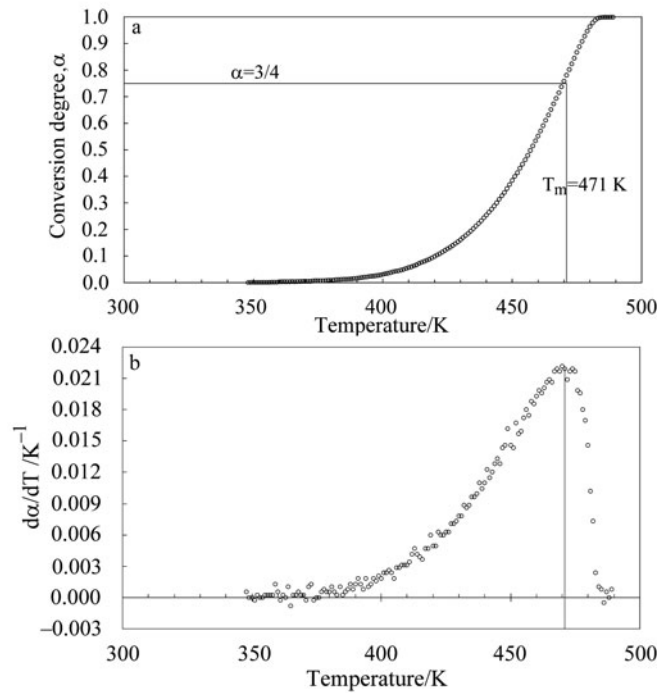


Fig. 3 a – Typical relationship between the conversion degree and temperature, a) and b – the relationship between the reaction rate ($d\alpha/dT = \Delta\alpha/\Delta T$) and temperature

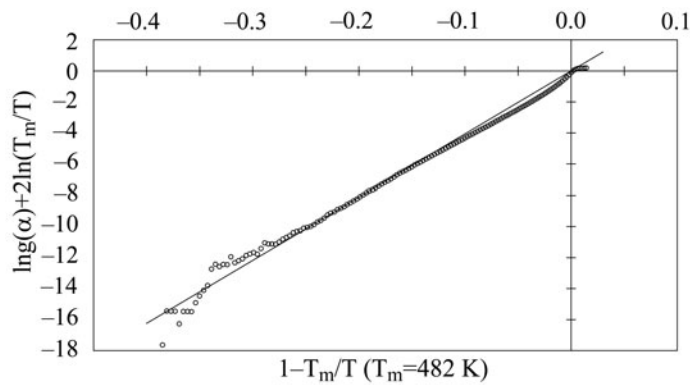


Fig. 4 Thermokinetic analysis of the conversion degree of the $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dehydration; data acc. [49] for of the best D3 model and Eq. (32) as a single parameter linear plot:

$$\ln(g(\alpha)) + 2\ln\frac{T_m}{T} = 40.60\left(1 - \frac{T_m}{T}\right), \quad g(\alpha) = \frac{3}{2}[1 - (1-\alpha)^{1/3}]^2$$

$$\bar{E} = \frac{40.6RT_m}{2} = 81350 \text{ J mol}^{-1} = 81.4 \text{ kJ mol}^{-1}, \quad \rho^2 = 99.74\%$$

reaction phase, when $\alpha \rightarrow 1$ [3, 49]. Further, we can conclude that if we can ‘substitute’ the diffusion models that are often used for the different ones of the R2 or R3 type then the problem analyzed in Table 1 practically disappears, i.e. there is no need to assume $\delta=1$ in condition (28) for the majority of $f(\alpha)$ functions. Figure 4 analyzes if condition (37) is fulfilled, in proviso that the above-mentioned condition of $\delta=1$ is obeyed. According to this criterion the best agreement is obtained for the R2 model, followed by the R3 model, while the diffusion models, including the best from Table 3 (D3), completely fail to obey the relationship.

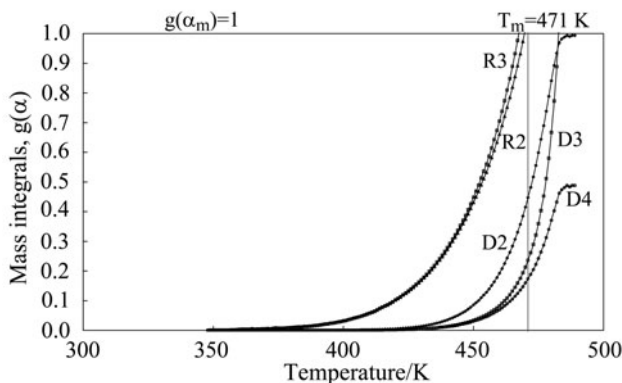


Fig. 5 The relationship between the mass integral and temperature for the D3, R3, D4, R2 and D2 models – the analysis of condition (37)

If we assume that we can make use of these equations which include the Kissinger law, (for example, Eq. (32)), the best approximation is obtained by introducing $T_m=482.0$ K, which means that it is 11 K higher than the actual one determined in the experiment. Thus we are obtaining the averaged value of activation energy of $E=81.4$ kJ mol⁻¹, which is higher than a value estimated to be a proper one (Table 3). Figure 5 shows the relationship of Eq. (32) which indicates that we can use the diffusion model (in a form of the combined thermokinetic equation and Kissinger law) but we should take into account that other thermokinetic data will bear an error, in this case – value T_m .

Supplement

It can be concluded from the analysis presented that it is very important for the Kissinger law given by (27) to obey a condition (30). This results in a fact that further Eqs (32) to (34) and (36) to (37) are all fulfilled. The initial point for this analysis is, however, the assumed thermokinetic equation (17).

Further, a solution of Eq. (18) gives:

$$g(\alpha) = \frac{A}{q} \int_0^T e^{-E/RT} \left(1 + \frac{E}{RT} \right) dT \quad (38)$$

It can be shown that the integral in the right side of this equation can be given by the elementary functions (Appendix 1).

Thus, once more we obtain Eq. (24), which appeared if we introduced relation (11) and the classical Arrhenius law to the Eq. (3), as discussed in details in [4].

From the analysis of the right hand side of Eq. (33) which is a modified form of (24) it can be concluded that Kissinger law introduced in a form of (31) makes it much more difficult to fulfill condition (37).

Summary I

The analysis of Eq. (17)

- 1) The $f(\alpha)$ or $g(\alpha)$ function should be selected, assuming numerical coefficients in them.
- 2) We make use of the Eqs (23) to (25) to obtain a series of kinetic parameters (E and A).
- 3) The obtained parameters form the isokinetic effect (of the C type according to [2]). Further, we estimate the provisional temperature of the maximal reaction rate T_m :

$$\frac{\partial \ln A}{\partial E} = \frac{1}{RT_m} \quad (39)$$

similarly as described previously [49], we calculate the averaged value of activation energy \bar{E} using the coefficients given in [9] and Table 3 (Appendix 2).

- 4) We assume that Kissinger law (27) and condition (30) is obeyed, i.e., $\delta=1$, to obtain (31) and further Eqs (32) to (34).
- 5) We assume that the $f(\alpha)$ functions for which condition (30) is not fulfilled, i.e., $\delta \neq 1$, (it is clear for R1, A1, 2F1–R1, D2, D3, D4 and conditionally D1) have the same meaning that the functions discussed in point 4.
- 6) If points 4 and 5 are true, then we can assume Eqs (31) and further (35)–(37).
- 7) According to point 6 it is possible to select the $f(\alpha)$ function among the best correlations, as comes from the statistical tests, e.g., [50] or Table 3.

However, we still cannot be sure if the kinetic parameters estimated (E and A) are true. It was postulated to present all thermokinetic equations that are properly fulfilled [51], while not caring about what the coefficients of the Arrhenius law represent.

The analysis of Eq. (18)

It is very difficult to justify a form of (18) of this equation, unless we a priori assume that Eq. (24) is obeyed. We cannot obtain any simple formula for condition (26), similar to this of Eq. (27).

The following equation is the equivalent of Eq. (27)

$$\frac{E^2}{R^2 T_m^3} - \delta \frac{A}{q} e^{-E/RT_m} \left(1 + \frac{E}{RT_m} \right)^2 = 0 \quad (40)$$

Further, for $\delta=1$ the equivalent of Eq. (31) takes a form of (Appendix 3):

$$\frac{A}{q} = \left(\frac{E}{E+RT_m} \right)^2 \frac{e^{E/RT_m}}{T_m} \quad (41)$$

By introducing Eq. (41) to Eq. (24) we obtain [52]

$$g(\alpha) = \left(\frac{T}{T_m} \right) \left(\frac{E}{E+RT_m} \right)^2 \exp \left[\frac{E}{RT_m} \left(1 - \frac{T_m}{T} \right) \right] \quad (42)$$

in proviso that

$$E \gg RT_m \text{ (e.g. } T_m = 500 \text{ K, } RT_m = 4.2 \text{ kJ mol}^{-1}) \quad (43)$$

Equation (42) simplifies to form:

$$g(\alpha) \cong \left(\frac{T}{T_m} \right) \exp \left[\frac{E}{RT_m} \left(1 - \frac{T_m}{T} \right) \right] \quad (44)$$

because

$$\left(\frac{E}{E+RT_m} \right)^2 \cong 1 \quad (45)$$

The solution given by Eqs (40) to (45) indicates a possibility for the generation of the further new forms derived from solutions Eqs (23) to (25), similarly to Eqs (32) to (34).

It can be shown that Eq. (24) is the solution of (17) [4, 5, 30, 36].

B/ Isokinetic effect

The analysis of Eq. (17) allows the possibility to include isokinetic effect (39), as discussed above. It usually admits a form of

$$\ln A = \frac{E}{RT_m} + \ln k_m, \quad q = \text{idem} > 0 \quad (46)$$

Also, the reaction rate constant k_m is determined by the Arrhenius equation which is fulfilled in any conditions, both isothermal ($T = \text{idem}$) and dynamic ones ($q = \text{idem} > 0$):

$$k_m = A e^{-E/RT_m} \quad (47)$$

Because T_m depends upon the heating rate according to (31) which can be given by

$$\ln \frac{q}{T_m^2} = \ln \frac{AR}{E} - \frac{E}{RT_m} \quad (48)$$

it is necessary to assume $q = \text{idem}$ in Eq. (46), as required by the Kissinger law.

From the point of view of mathematical formalism Eqs (46) and (47) are identical. They are however different if we indicate which of the variables is the dependent one and which is the independent one. Equation (46) can be obtained using a variety of the $f(\alpha)$ and $g(\alpha)$ functions, i.e., $\ln A$ vs. E . Equation (47) is a calculation formula which allow to calculate k_m if we know A , E and T_m .

If we introduce (31) into Eq. (46) we obtain the following relationship [30]:

$$\ln A = \frac{E}{RT_m} + \ln \frac{qE}{RT_m^2} \quad (49)$$

which implies

$$k_m = \frac{qE}{RT_m^2} \quad (50)$$

Relationship (50) can be shown in a form involving dimensionless activation energy ($u_m = E/RT_m$):

$$k_m = \frac{q}{T_m} u_m \quad (51)$$

At least three cases can be indicated:

- 1) $k_m = \text{idem}$,
- 2) $k_m \neq \text{idem}$, in proviso that the formula is fulfilled
or
- 3) the formula is not fulfilled.

More assumptions are needed for both the right and left sides of (51) in order to discuss it further. Such a complex analysis indicates that the connection of Kissinger law and isokinetic effect (of the C type according to [2]) brings a contradiction.

To solve this problem we assume that

- i*) there is any true formula among (23) to (25),
- ii*) condition (37) is fulfilled for all $g(\alpha)$ (according to Table 1 only the D4 model is excluded),
- iii*) the Arrhenius equation in a form of (47) is true.

Putting all these together, if $g(\alpha_m) = 1$, we obtain following forms:

from (23) Eq. (50)

$$\text{from (24)} \quad k_m = \frac{q}{T_m} \quad (52)$$

$$\text{from (25)} \quad k_m \cong \frac{qR}{0.005E} \quad (53)$$

Further procedure involves

- a*) the determination of the k_m according to (46),
- b*) the analysis of the single-parameter correlation

k_m vs. q/T_m^p , where $p=2, 1$ or 0 (for $p=1$, slope=1)

c) the comparison of the determined values of activation energy with the actual ones, assuming the averaged \bar{E} value and the Kissinger law for the different heating rates q .

A priori, we can reject Eqs (50) or (51), because both introduce inconsistency. The same applies to Eq. (53) which does not guarantee the agreement with activation energy E .

In this context, Eq. (52) seems to be the most reliable and secure, because it does not contain a term of activation energy, therefore, it seems to prove that Eq. (24) should be used in dynamic conditions, despite the fact that it is Eq. (23) that is most used.

Summary II

A discussion of the precision of the Kissinger law and isokinetic effect, if applied together at the same time, results in a conclusion that these equations are connected only by Eq. (24). It is true however only in proviso that we assume the modified version of the Kissinger law.

If we modified the left side of Eq. (52) to a form of

$$Ae^{-E/RT_m} = \frac{q}{T_m} \quad (54)$$

we obtain:

$$\ln\left(\frac{q}{T_m}\right) = \ln A - \frac{E}{RT_m} \quad (55)$$

We can observe that introducing simplified representation (45) to Eq. (41) once more we obtain (55), which concludes our analysis of the strictly defined cycle.

Theoretical analysis enabled us to perform further investigations into the correctness of Eqs (50) to (53), which were presented elsewhere [53].

Conclusions

It is very strange that the first IUPAC publication from 1981 [54] does not mention anything about the definitions of the terms used in chemical kinetics (as well as recommended symbols) of dynamic conditions. Our analysis shows that there are still many controversies in this field, which concerns very substantial problems. Basically, ICTAC Conference [13–17] concentrates on the analysis of ‘a single kinetic triplet’ [14]: E , A and $f(\alpha)$ in the different experimental conditions of decomposition, basing mainly on the differentials according to Eq. (12). However, a number of the specific problems concerning dynamic conditions have been omitted. We tried to discuss these issues in the current work. The dilemmas remaining are to be resolved by the individual Reader on his own.

Table 4 The reactions between thermokinetic equations and the Kissinger law and isokinetic effect

Differential equations	Integral equations	Other laws
$\frac{d\alpha}{dT} = \frac{A}{q} e^{-E/RT} f(\alpha),$ $q > 0 \text{ (17) accurate}$	$g(\alpha) = \frac{ART^2}{qE} e^{-E/RT} \text{ (23)}$ <p>approximate</p>	—
$\frac{d\alpha}{dT} = \frac{A}{q} e^{-E/RT} f(\alpha) \left(1 + \frac{E}{RT} \right),$ $q > 0 \text{ (18) accurate}$	$g(\alpha) = \frac{AT}{q} e^{-E/RT} \text{ (24)}$ <p>accurate</p> <p>(24)</p> <p>Ia accurate: acc. [4, 5], Ib accurate: combination of Eqs (3), (11) and classical Arrhenius law, II approximate acc. [30]</p>	—
(17) accurate		—
—	—	Kissinger law $\delta = 1, \frac{A}{q} = \frac{E}{RT_m^2} e^{E/RT_m} \text{ (31)}$
—	—	isokinetic effect $\ln A = \frac{E}{RT_m} + \ln k_m, q = \text{idem} \text{ (46)}$
$\frac{d\alpha}{dT} = f(\alpha) e^{(E/RT_m)(1-T_m/T)} \frac{E+2RT}{RT_m^2}$ <p>approximate</p>	<p>we introduce (31) to Eq. (23) to obtain</p> $g(\alpha) = \left(\frac{T}{T_m} \right)^2 e^{(E/RT_m)(1-T_m/T)} \text{ (32)}$ <p>approximate</p>	—
—	—	from Eq. (32): $T = T_m, g(\alpha_m) = 1$
—	—	in Eq. (24) we assume $g(\alpha_m) = 1, T = T_m, k_m = q/T_m$ together with the Arrhenius law we are obtaining $\ln \frac{q}{T_m} = \ln A - \frac{E}{RT_m} \text{ (55)}$

The current work indicates that Eq. (24) is validated from the point of view of the Kissinger law in its (55) version and isokinetic effect, despite a fact that its differential form (18) differs from the basic notation (17).

Thus, if we assume that Eq. (24) is validated we obtain a simple relationship (52), which determines the rate constant of the decay reaction at the temperature where the rate takes a maximal value, i.e., $k_m=q/T_m$.

The most important conclusions of the current work were shown in Table 4.

List of symbols

A	pre-exponential factor/min ⁻¹
b	the coefficient for converting activation energy E
C	a constant that can take a value given by Eqs (32) to (34)
$e=$	2.718
E	activation energy/J mol ⁻¹
\bar{E}	averaged value of activation energy/J mol ⁻¹
$f(\alpha)$	symbol of the mechanism of reaction/process
$g(\alpha)$	mass integral
ΔG	free enthalpy/J mol ⁻¹
$h(\alpha)$	a derivative of the $f(\alpha)$ function according to (29)
ΔH	enthalpy/J mol ⁻¹
k	rate constant/min ⁻¹
$k(T)$	rate constant depended on T /min ⁻¹
m	a coefficient that can take a constant value of $m=2, 1$ or 0
n	the reaction order
p	exponent ($p=2, 1$ or 0)
$R=$	8.314 J mol ⁻¹ K ⁻¹
r^2, ρ^2	determination coefficient for the double and single parameter linear plot, respectively/%
q	heating rate/K min ⁻¹
T	absolute temperature/K
T_m	temperature of the maximal rate reaction/process, from condition (26)/K
u	dimensionless activation energy
α	conversion degree, $0 \leq \alpha \leq 1$
δ	a specific value of the $h(\alpha)$ function
v	stoichiometric coefficient
η	thermodynamic yield, $0 \leq \eta \leq 1$
τ	time/min

Indexes

d	decomposition
eq	equilibrium
i	initial state
m	maximal reaction rate
min	minimum

The kinetic function symbols that were in Tables 1 to 3 were given according to [2, 49].

Appendix 1

In Eq. (38) we substitute $E/RT=x$, $dT=-\frac{E}{R} \frac{dx}{x^2}$
to obtain $g(\alpha)=\frac{A}{q} J$

where

$$J=\frac{E}{R} \int_0^{\infty} \left(\frac{e^{-x}}{x^2} + \frac{e^{-x}}{x} \right) dx \quad (\text{A1})$$

This we can further present in a form of

$$J=\frac{E}{R} (J_1+J_2) \quad (\text{A2})$$

The J_1 and J_2 integrals cannot be given by the elementary integrals, but we can obtain such a form for their sum to obtain

$$J_1=\int_x^{\infty} \frac{e^{-x}}{x^2} dx = -\frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-x}}{x} dx \quad (\text{A3})$$

$$J_2=\int_x^{\infty} \frac{e^{-x}}{x} dx \quad (\text{A4})$$

which after putting together gives

$$J_1+J_2 = -\frac{e^{-x}}{x} \Big|_x^{\infty} = \frac{RT}{E} e^{-E/RT} \quad (\text{A5})$$

The solutions of the J_1 and J_2 integrals appeared to be consistent with Tables presented in [55] and previously works published by Błażejowski [4, 7, 32].

Appendix 2

The term of the averaged activation energy was defined in [9] and the current work.

If we do not take into account the Doyle's coefficient of 1.0516, we should bear in mind that

1) if we start from the temperature criterion

$$\ln \alpha \text{ vs. } 1/T \quad (\text{A6})$$

the activation energy [35] values must be multiplied by the b coefficient that is given in [9].

2) during the analysis of thermokinetic models in a version of

$$\ln \frac{g(\alpha)}{T^m} \text{ vs. } 1/T, m=2, 1 \text{ or } 0 \quad (\text{A7})$$

the activation energy values must be divided by the b coefficient.

For further example compare Table 1 [3].

Appendix 3

We start from Eq. (18) obtaining for condition (26)

$$\begin{aligned} \frac{d^2\alpha}{dT^2} &= \frac{d^2\alpha_m}{dT_m^2} = \\ &= \frac{A}{q} e^{-E/RT_m} \left\{ \left[f(\alpha_m) \frac{E}{RT_m^2} + \frac{df(\alpha_m)}{d\alpha_m} \frac{d\alpha_m}{dT_m} \right] \left(1 + \frac{E}{RT_m} \right) - f(\alpha_m) \frac{E}{RT_m^2} \right\} = 0 \end{aligned} \quad (\text{A8})$$

Substitution into (A8) for $[df(\alpha_m)/d\alpha_m]$ Eq. (28) with condition (30), and for $(d\alpha_m/dT_m)$ Eq. (18) we obtain:

$$\frac{A}{q} e^{-E/RT_m} f(\alpha_m) \left[\frac{E}{RT_m^2} \left(1 + \frac{E}{RT_m} \right) - \frac{A}{q} e^{-E/RT_m} \left(1 + \frac{E}{RT_m} \right)^2 - \frac{E}{RT_m^2} \right] = 0 \quad (\text{A9})$$

After final putting in order we obtain Eq. (41).

* * *

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