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A new approach to solid-state reactions kinetics analysis: the application of assisting functions to basic equations for isothermal conditions

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Abstract

Functions describing simple models for solid-state reaction kinetics under isothermal conditions were transformed in order to obtain new functions with improved properties suitable for kinetic analysis. The transformations were performed trough multiplying well known functions as Johnson–Mehl–Avrami or Jander's with assisting functions. In such manner, new functions, Φ, were obtained enabling calculation of kinetic parameters in a simple way.

The relationships between the values of the extremes of Φ functions and various kinetic parameters have been established. The calculation of kinetic parameters by application of new equations have been demonstrated on six model systems. Very good agreement between preset and calculated parameters for each model system has been observed.

Using the same approach, the rate-determining step, i.e. the reaction model, and proper kinetic equation could also be determined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the purposes of kinetic studies is to find the most probable course of reaction; in other words, to obtain insight into a reaction mechanism. It is usual to postulate a model for reaction, which depends on the rate-determining step. The models which have been proposed for solid-state reactions can be divided into three major groups: (a) diffusion models, D [1–3], (b) phase boundary models, PB [4,5] and (c) nucleation and growth models, NG [6–14]. When a model is postulated the next goal is to determine the kinetic parameters, which is most often done by analytical methods. At present, indebted to readily available computation power, the numerical methods are often employed [15–17].

However, the functions that describe any model might be transformed, in order to obtain new functions with improved properties suitable for kinetic analysis. Such new approach is elaborated in this work. It may also be useful in those cases where standard, unmodified functions are readily applicable.

2. Theoretical

The functions supposed to describe mathematically experimental kinetic curves can be divided in two

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major groups: integral and differential functions. For instance, the phase boundary model is often described with the integral equation [4]

$$g(\alpha) = 1 - (1 - \alpha)^{1/3} = kt \quad (1)$$

or explicitly

$$g(t) = 1 - (1 - kt)^3 = \alpha \quad (2)$$

where α is the volume fraction transformed, k the rate constant and t is the time.

In differential form, the same equation reads as

$$f(\alpha) = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = 3k(1 - \alpha)^{2/3} \quad (3)$$

or

$$f(t) = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = 3k(1 - kt)^2 \quad (4)$$

The selection of mathematical form (integral or differential) usually depends on experimental data obtained. For instance, if X-ray diffraction is used in order to study transformation kinetics, the $\alpha - t$ dependence, typical for integral form, is obtained. On the other hand, the employment of differential scanning calorimetry results with differential $(\mathrm{d}\alpha/\mathrm{d}t) - t$ dependence.

2.1. The definitions of the new functions, Φ

Regardless of form, any function F, that is supposed to describe any model for solid-state reaction kinetics, could be transformed. The goal of such treatment is to obtain the functions Φ, with improved properties, favorable for kinetic analysis. For instance, function F could be multiplied with any other function, i.e. assisting function, φ.

$$\Phi = F\varphi. \quad (5)$$

In such manner, new function Φ, is obtained having new properties and being completely different from F function, but influenced by functions F and φ. If the function φ is suitably chosen it is possible to obtain such form of function F that enables easier determination of kinetic parameters; if the experimentally obtained curve obeys particular function, its transformed form will enable calculation of kinetic parameters in a simple manner. Moreover, using the same approach, the rate-determining step, i.e. the reaction model, and proper kinetic equation could also be determined.

The φ function could have various forms. Form that enables obtaining of Φ function with predicted characteristics has to be selected. In this work, the φ function has been selected in order to obtain the Φ function that has maximal value in the range of interest, regardless weather the function F has extreme in that range. For instance, the differential function describing the nucleation and growth process has an extreme, while the functions for the processes limited by diffusion or reaction at the interface are monotonously decreasing ones. Simple function, $\varphi = t^m$ (where m has to be restricted depending on function F), that fulfil such criteria, is selected.

Let us consider, how the function $\varphi = t^m$ influence to the properties of some, well known differential or integral forms of functions for nucleation and growth, phase boundary and diffusion limited models.

2.2. Differential functions

The differential form of Johnson–Mehl–Avrami equation, the most often used to describe nucleation and growth mechanism, reads as

$$F = f(t) = nk^n t^{n-1} \exp[-(kt)^n] \quad (6)$$

where n is the Avrami exponent.

With $\varphi = t^m$, the Φ function reads as

$$\Phi(t, m) = nk^n t^{m+n-1} \exp[-(kt)^n] \quad (7)$$

The function Φ has its maximum at $t = t_{\mathrm{p}}(m)$ which depends on m, k and n. For $\mathrm{d}\Phi/\mathrm{d}t = 0$, one obtains (Appendix A)

$$kt_{\mathrm{p}}(m) = \left(\frac{m + n - 1}{n}\right)^{1/n} \quad (8)$$

where $m > (1 - n)$.

The differential form of equation describing phase boundary model reads as

$$F = f(t) = nk(1 - kt)^{n-1} \quad (9)$$

where $n = 3$ for three-dimensional process and $n = 2$ for two-dimensional process.

In this case, with $\varphi = t^m$, we have the following Φ function:

$$\Phi(t, m) = nkt^m(1 - kt)^{n-1} \quad (10)$$

which has its maxima at

$$kt_{\mathrm{p}}(m) = \left(\frac{m}{m+n-1}\right) \tag{11}$$

where $m > 0$.

The differential form of Jander equation describing the diffusion mechanism reads as

$$F = f(t) = \frac{3}{2}\frac{k[1-(kt)^{1/2}]^2}{(kt)^{1/2}} \tag{12}$$

with $\varphi = t^m$ the Φ function will be

$$\Phi(t,m) = \frac{3}{2}kt^m\frac{[1-(kt)^{1/2}]^2}{(kt)^{1/2}} \tag{13}$$

having its maxima at

$$kt_{\mathrm{p}}(m) = \left(\frac{2m-1}{2m+1}\right)^2 \tag{14}$$

where $m > 0.5$.

In such manner, the functions $\Phi(t, m)$ that have maxima defined by process (function F), kinetic parameters (rate constant and dimensionless constants) and selected m constant (in φ function), are obtained. Although the original functions, F, for diffusion and phase boundary limited process (Eqs. (9) and (12)) have no maxima for $t > 0$, each $\Phi(t, m)$ function has its maximum, $t_{\mathrm{p}}(m)$, according to the Eqs. (11) and (14). The computer-generated curves of the above Φ functions, with various m values, are shown in Fig. 1.

2.3. Integral functions

$\alpha - t$ dependence are described by integral functions. For the majority of the integral functions in explicit form, the application of the function $\varphi = t^m$ would not be of use because multiplication of explicit form of integral equations (e.g. Eq. (2)), with $\varphi = t^m$ gave Φ functions without maxima. However, if the functions F are defined as $F = (1 - \alpha)$, the functions $\Phi = F\varphi$, where $\varphi = t^m$ will have maxima. The influence of function $\varphi = t^m$ on integral form of previously reviewed functions is given as follows.

The integral form of Johnson–Mehl–Avrami equation [9] reads as

$$F = g(t) = (1-\alpha) = \exp[-(kt)^n] \tag{15}$$

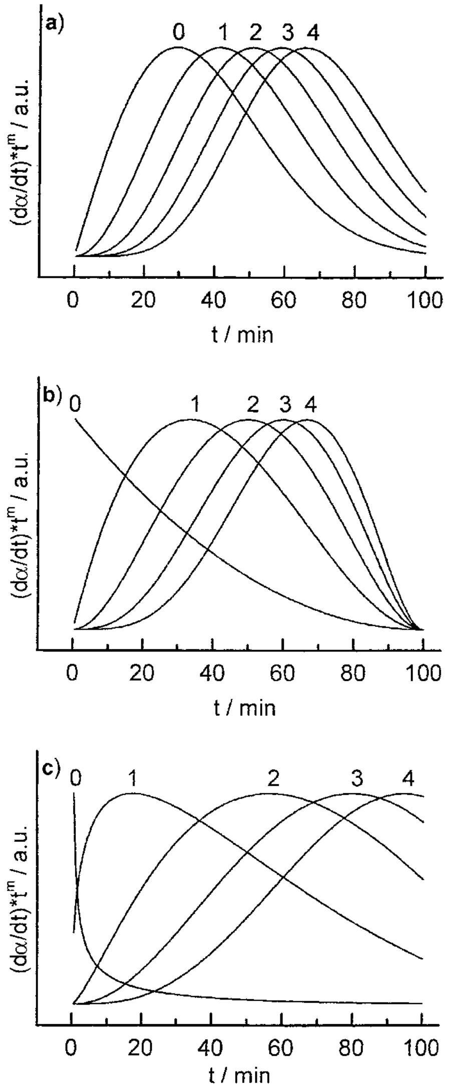

Fig. 1. Model systems curves simulated upon kinetic models and parameters shown in Table 1, and their normalized Φ curves obtained by multiplying simulated data with t^m ($m = 0$–4): (a) model system S1; (b) model system S2; (c) model system S3.

with $\varphi = t^m$, the proper Φ function is obtained:

$$\Phi(t,m) = (1-\alpha)t^m = t^m\exp[-(kt)^n] \tag{16}$$

The function Φ has its maxima at $t = t_{\mathrm{p}}(m)$ which depends on m, k and n. For $\mathrm{d}\Phi/\mathrm{d}t = 0$:

$$kt_{\mathrm{p}}(m) = \left(\frac{m}{n}\right)^{1/n} \tag{17}$$

where $m > 0$.

The integral form of equation describing phase boundary model [4] reads as

$$F = g(t) = (1 - \alpha) = (1 - kt)^n \tag{18}$$

with $n = 3$ for three-dimensional process and $n = 2$ for two-dimensional process.

By applying $\varphi = t^m$, the Φ function will be

$$\Phi(t, m) = (1 - \alpha)t^m = t^m(1 - kt)^n \tag{19}$$

having its maximum at

$$kt_p(m) = \left(\frac{m}{m + n}\right) \tag{20}$$

where $m > 0$.

The integral form of Jander equation [1] is

$$F = g(t) = (1 - \alpha) = [1 - (kt)^{1/2}]^3 \tag{21}$$

Using of $\varphi = t^m$ will give Φ function:

$$\Phi(t) = (1 - \alpha)t^m = t^m[1 - (kt)^{1/2}]^3 \tag{22}$$

with maxima at

$$kt_p(m) = \left(\frac{2m}{2m + 3}\right)^2 \tag{23}$$

where $m > 0$.

The computer-generated curves of the above Φ functions, with various m values, are shown in Fig. 2.

The derived equations enable the calculation of the rate constants and dimensionless constants. The t_p for the curves obtained with various m values have to be calculated first. From the obtained sets of $m - t_p$ data, mentioned kinetic parameters are obtained through simple relationships.

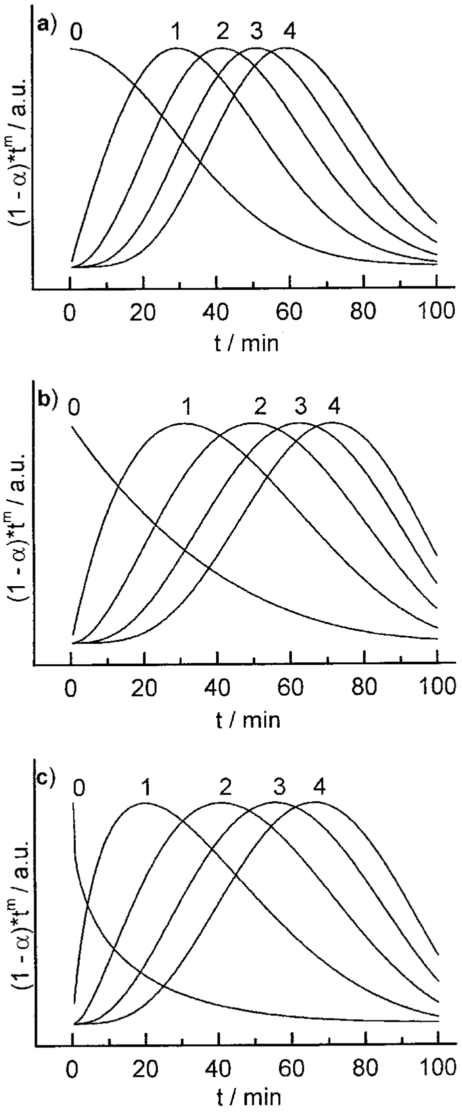

Fig. 2. Model systems curves simulated upon kinetic models and parameters shown in Table 1, and their normalized Φ curves obtained by multiplying simulated data with t^m ($m = 0$–4): (a) model system S4; (b) model system S5; (c) model system S6.

2.4. The Arrhenius equation

From Eqs. (8), (11), (14), (17), (20) and (23), it could be seen that the expressions for extreme of the function Φ have the same, characteristic form

$$kt_p(m) = C \tag{24}$$

Eq. (24) is satisfied if F is given explicitly, i.e. if $F = (d\alpha/dt) = f(t)$ or $F = (1 - \alpha) = 1 - g(t)$. Constant C depends on functions that describe process, and on parameters m and n (NG and PB), but does not depend on temperature. The equation for isothermal processes at different temperatures could be expressed as

$$k(T)t_p(T, m) = C \tag{25}$$

By introducing Arrhenius equation to Eq. (25), the relation is obtained

$$k_0 t_p(T, m) \exp\left(-\frac{E}{RT}\right) = C \tag{26}$$

which is in logarithm form suitable for calculation of the activation energy

$$\ln[t_p(T, m)] = C^* + \frac{E}{RT} \tag{27}$$

Similar equation is given by Kemeny and Šestak [18], but only for JMA function.

The advantage of using Eq. (27) instead of standard procedure for calculation of activation energy through rate constants lays in fact that it is not necessary to know which process is rate limiting for the reaction in the solid-state. The determination of $t_p(T, m)$, i.e. the maxima of Φ function for various temperatures and the same m value provides all the necessary data for activation energy calculation. Use of any m should give the same linear relationship, i.e. straight lines with the same slope. In the case of application on experimental data, it is necessary to include the standard regression analysis, as well as test for parallelism. If the straight lines have not the same slope, function F is more complex than it has been assumed. The procedure is similar to the situation in isoconversional method recommended by Šestak and Malek [19].

2.5. The functions for discerning the rate-determining step

Equations given in Sections 2.2 and 2.3 usually serve for the calculation of kinetic parameters, under assumption that the applied kinetic model is correctly proposed. If the reaction mechanism is not previously known or determined, the experimental data have to be tested, in order to discern the rate-determining step, i.e. the reaction model and proper kinetic equation. The equations for this testing are more complicated than those in Sections 2.2 and 2.3. They are derived for analysis of differential forms of kinetic functions only, with an aim to select the rate-determining process by evaluation of characteristic parameters. The general form of these equations is

$$F = \frac{d\alpha}{dt} = H_1^p H_2^q \tag{28}$$

where H_1 and H_2 are functions of α or t, and p and q characteristic parameters.

Function F can be transformed as shown in Sections 2.2–2.4. Two different functions will be treated in this work. They are

$$F = (1-\alpha)^p[-\ln(1-\alpha)]^q \tag{29}$$

$$F = (1-\alpha)^p[1-(1-\alpha)^{1/3}]^q \tag{30}$$

Function F (Eq. (29); identical as in Appendix B) has been used most frequently for testing of experimental data. When experimental data obey JMA function (Eq. (15)) $p = 1$ and $q < 1$ will satisfy the equation. If $q = 0$ and $p = 1/2$ or $2/3$, experimental data will obey phase boundary models (Eq. (18)). Eq. (30) can be decisive in the selection between chemical reaction on the interface with $q = 0$ and $p = 1/2$ or $2/3$ and diffusion with $q = -1$ and $p = 2/3$ (Jander's equation), or with $q = -1$ and $p = 1/3$ (Ginstling and Brounstein's equation).

Any deviation from the above values for parameters q and p calls for caution in the determination of the rate-determining processes. In this case, the proper kinetic equation is probably more complex than the equations treated in this work. In Eqs. (28)–(30), F depends on α. Therefore, it will be convenient to operate with assisting function which also depends on α, i.e. with $\varphi = \alpha^m$. The assisting function $\varphi = \alpha^m$ may be useful for application in analysis of the three considered processes (NG, PB and D), because it gives the corresponding Φ functions with the extremes that depend on m.

Eq. (28) can also be transformed like all the other functions from Sections 2.2 and 2.3; testing functions can be multiplied by the assisting function in order to determine maxima of Φ functions $d\Phi/d\alpha = 0$. This treatment gives new characteristic functions which are in fact linearized testing functions. Their general forms reads (Appendix C) as

$$Y = pX_1 + qX_2 \tag{31}$$

Consequently, the parameters p and q will be obtained by the multiple linear regression. By using $\varphi = \alpha^m$, the transformed form of Eq. (29) is

$$X_1 = \alpha_p(m)[-\ln(1-\alpha_p(m))] \tag{32}$$

$$X_2 = -\alpha_p(m) \tag{33}$$

$$Y = m(1-\alpha_p(m))[-\ln(1-\alpha_p(m))] \tag{34}$$

whilst for Eq. (30) one obtains

$$X_1 = -\alpha_p(m)[1-(1-\alpha_p(m))^{1/3}] \tag{35}$$

$$X_2 = -\tfrac{1}{3}[1-\alpha_p(m)]^{1/3} \tag{36}$$

$$Y = m[1-\alpha_p(m)][1-(1-\alpha_p(m))^{1/3}] \tag{37}$$

Thus, by applying the proper assisting function, the characteristic equation can be derived for any testing function.

3. Results and discussion

With the purpose of testing, the validity of proposed method for the determination of kinetic parameters, the model systems named S1 to S6 were formed. The kinetic models and kinetic parameters used for creating model systems are shown in Table 1. Using functions and parameters presented in Table 1, sets of $\mathrm{d}\alpha/\mathrm{d}t - t$ (Fig. 1, $m = 0$) and $(1-\alpha) - t$ (Fig. 2, $m = 0$) data were generated.

The function t^m was taken as φ function, the m values used for calculation are given in Table 2. The Φ curves were obtained by multiplying data columns, $\mathrm{d}\alpha/\mathrm{d}t$ or $1-\alpha$, with mth powered t columns. This procedure was performed trough self-designed computer routine, but it could be performed with any spreadsheet computer application. The normalized Φ curves ($\Phi_{\max} = 1$) for $m = 1$–4 are presented in Figs. 1 and 2 and t_p values for curves obtained using various m values are shown in Table 2.

The rate constant and Avrami exponent for model system S1 were calculated as follows: if the m in Eq. (8) is chosen to be 1, the equation reads as

$$kt_p(m = 1) = 1 \tag{38}$$

Table 1
Kinetic models and parameters used for creating of model systems

Model system	Kinetic model	Mathematical form	Equation number	Parameters	
				k (min^{-1})	n
S1	Nucleation and growth	Differential	(6)	0.024	2
S2	Phase boundary		(9)	0.01	3
S3	Diffusion limited		(12)	0.0064	–
S4	Nucleation and growth	Integral	(15)	0.024	2
S5	Phase boundary		(18)	0.008	3
S6	Diffusion limited		(21)	0.008	–

Table 2
Obtained t_p values (in minutes) for model systems and Φ curves, calculated rate and dimensionless constants

m	Model system					
	S1	S2	S3	S4	S5	S6
0	29	0	0	0	0	0
1	42	34	17.5	29	31	20
1.25	44.5	37.5	29.5	33	36.5	25.5
1.5	46.5	42	39	36	42	31
1.75	49	46	48.5	39	46	36
2	51	50	54	41.5	50.5	41
2.5	55.5	56	68.5	46.5	56.5	49
3	59.5	60	80.5	51	62.5	56
3.5	62.5	64	89	55	67	62.5
4	65.5	66	95	59	71	65.5
k (min^{-1})	0.0238	0.0101	0.0064	0.024	0.0079	0.0080
n	2.0	3.0	–	2.0	3.1	–

which means that for $m = 1$, the t_p, instead on k and n, depends only on k (it is worth noting that for $m = 1$ $\alpha_p = 0.632$). Therefore, rate constant for model system S1 was calculated using $t_p(m = 1)$ only (Table 2). By division of Eq. (38) ($m = 1$) with Eq. (8) for $m = 0$, the following relation is obtained:

$$\frac{t_p(0)}{t_p(1)} = \left(\frac{n-1}{n}\right)^{1/n} \tag{39}$$

By using measured $t_p(0)$ (the experimental peak maxima) and calculated $t_p(1)$ the Avrami exponent for model system S1 has been determined trough simple iteration procedure (Table 2).

For model system S2, according to Eq. (11), a linear dependence $1/t_p(m)$ versus $1/m$ was obtained, and the rate constant was calculated from the intercept. With known k, the process geometry was calculated from the slope (Table 2).

For model system S3, according to Eq. (14), a linear dependence $t_p(m)$ versus $[(2m-1)/(2m+1)]^2$ was obtained. The rate constant were calculated from the slope and presented in Table 2.

It could be shown from Eq. (17) that

$$\ln\frac{m_1}{m_2} = n\ln\frac{t_p(m_1)}{t_p(m_2)} \tag{40}$$

Using Eq. (40), the Avrami exponent for model system S4 was calculated; with the known Avrami exponent the rate constant was obtained from Eq. (17). The calculated values are shown in Table 2.

According to Eq. (20), a linear dependence $1/t_p(m)$ versus $1/m$ was obtained for model system S5, and the rate constant was calculated from the intercept. With the known k, the geometry constant was calculated from the slope (Table 2).

According to Eq. (23), a linear dependence $t_p(m)$ versus $[2m/(2m+3)]^2$ was obtained for model system S6 and the rate constant was calculated from line slope. The calculated rate constant is shown in Table 2.

As can be seen from Table 2, very good agreement between preset and calculated parameters is observed for each model system.

The rate of volume fraction transformed for model system S1 is computed for a different temperatures, with

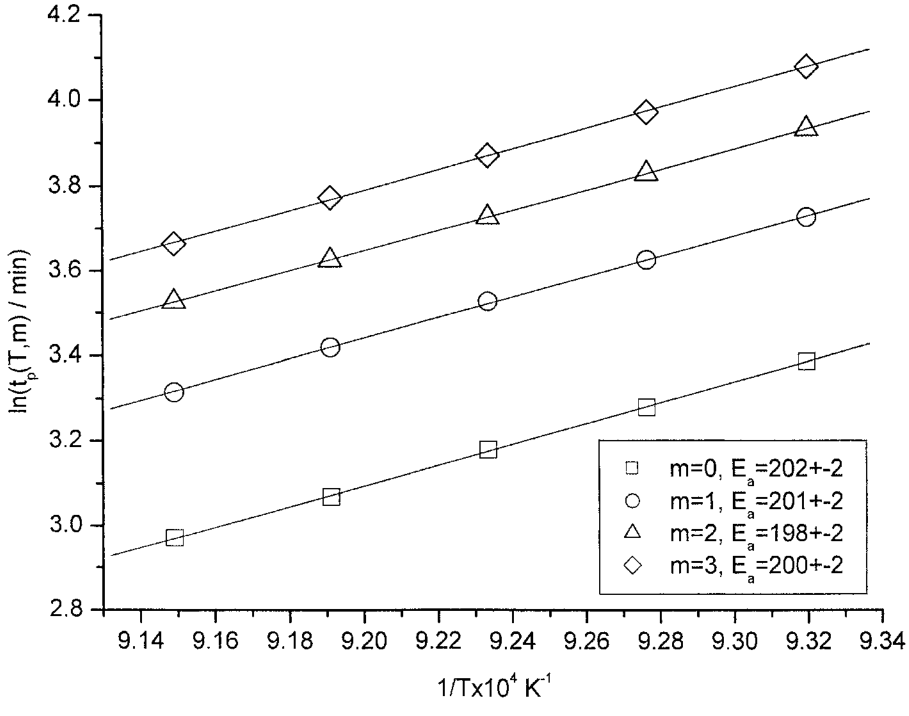

Fig. 3. Plots of ln $t_p(m)$ vs. $1/T$ for the curves of model system S1 computed for various temperatures.

Table 3
The $t_p(T, m)$ values (in minutes) for model system S1 curves simulated for a different temperatures (using $E_a = 200\ \text{kJ mol}^{-1}$, $n = 2$, $k_0 = 1.31 \times 10^8\ \text{min}^{-1}$) ($m = 0$) and the appropriate Φ curves ($m = 1$–3), and the activation energies calculated from Eq. (27)

m	T (°C)					E_a (kJ mol^{-1})
	800	805	810	815	820	
0	29.5	26.5	24.0	21.5	19.5	202 ± 2
1	41.5	37.5	34.0	30.5	27.5	201 ± 2
2	51.0	46.0	41.5	37.5	34.0	198 ± 2
3	59.0	53.0	48.0	43.5	39.0	200 ± 2

$E_a = 200\ \text{kJ mol}^{-1}, n = 2$ and $k_0 = 1.31 \times 10^8\ \text{min}^{-1}$. The temperatures and the obtained $t_p(T, m)$ values for $m = 0$–3 are presented in Table 3. According to Eq. (27), linear dependences $\ln t_p(T, m)$ versus $1/T$, were obtained (Fig. 3) and activation energies were calculated from each slope (Table 3). As can be seen from Table 3, very close values for activation energies and a match with preset E_a were obtained, and good agreement between preset and calculated parameters is observed for each model system.

The testing of rate-determining step is performed by multiplying the previously described S1 to S3 curves with $\varphi = a^m$ for different m values (Table 4). According to Eqs. (29) and (30), p and q were obtained by multiple linear regression. In Table 5, the results of testing are shown. The obtained p and q values clearly point out to the proper kinetic functions.

Table 4
The α_p values obtained for model systems S1 to S3 using function $\varphi = \alpha^m$

m	S1	S2[a]	S3[a]
−0.4	0.114		
−0.25	0.283		
0	0.396		
0.25	0.488	0.271	
0.5	0.567	0.428	
0.75		0.525	0.150
1	0.657	0.603	0.156
1.25		0.65	0.22
1.5	0.715	0.692	0.362
1.75		0.725	0.448
2	0.759	0.75	0.527
2.5	0.792	0.789	0.617
3	0.816	0.82	0.697
4			0.781
5			0.825

[a] Curve S2 has no maxima for $m < 0$ and S3 for $m < 0.5$.

Table 5
The results of rate-determining step testing using two different models

	Curve			
	S1	S2	S2	S3
	Eq. (29)		Eq.(30)	
p	0.96	0.66	0.66	0.65
q	0.47	−0.01	−0.01	−0.96
S.D. × 10^2	0.972	0.337	0.311	0.089
p^a	1.00	0.67	0.67	0.67
q^a	0.50	0	0	−1.00

[a] Preset parameters.

Table 6
Equations for calculations of the kinetic parameters through α_p

Kinetic model	Mathematical form	Equation	Condition	Derived from
Nucleation and growth	Differential	$-\ln[1 - \alpha_p(m)] = \dfrac{m + n - 1}{n}$	$m > (1 - n)$	Eqs. (8) and (15)
Phase boundary		$1 - \alpha_p(m) = \left(\dfrac{n - 1}{m + n - 1}\right)^n$	$m > 0$	Eqs. (11) and (18)
Diffusion limited		$1 - \alpha_p(m) = \left(\dfrac{2}{2m + 1}\right)^3$	$m > 0.5$	Eqs. (14) and (21)
Nucleation and growth	Integral	$-\ln[1 - \alpha_p(m)] = \dfrac{m}{n}$	$m > 0$	Eqs. (15) and (17)
Phase boundary		$1 - \alpha_p(m) = \left(\dfrac{n}{m + n}\right)^n$	$m > 0$	Eqs. (18) and (20)
Diffusion limited		$1 - \alpha_p(m) = \left(\dfrac{3}{2m + 3}\right)^3$	$m > 0$	Eqs. (21), (23)

In the same way as the functions, the experimentally obtained curves, supposed to obey particular function, could be transformed. Such procedure could be easily carried out by any spreadsheet computer application. The procedure is no more complicated than the classical analysis of isothermal experiment data. For the data analysis of some experimental methods, e.g. DSC, it is even less complicated, since there is no need for calculation of the volume transformed. Method is especially valuable for the activation energy calculation, since process rate-determining step does not have to be known.

From theoretical consideration and from results of analysis of the model systems, the relationships between the values determined by extremes of Φ functions and various kinetic parameters have been established. Also, the equation enabling calculation of kinetic parameters from extreme values have been performed. As shown in Table 6, new relations could be obtained, where instead of t_p, α_p parameter is included.

4. Conclusions

Functions representing different kinetic models for isothermal conditions, were transformed in order to create new functions with properties that enable different approach to kinetic analysis. The transformation is performed by multiplying the function that represent the kinetic model, *F*, with assisting function, φ. The selection of the function φ depends on the type of experimental results and has to be chosen in such manner that transformed curve, Φ, has a maximum.

Function Φ is not a kinetic function. It is not characterized by integral or differential form, and does not appear as a result of process analysis. But this function involves all the kinetic parameters characteristic for F function, and interconnects them as demanded by the assisting function φ and its parameters (e.g. m).

By introducing of Φ functions the great number of relations between kinetic parameters and parameters of φ function is obtained. This increased number of relations enables enhanced reliability in determination of kinetic parameters.

It is worth noting that although only the curve extremes are employed in discerning of the kinetic parameters, the major part of a curve is represented, since the different parts of the curve are employed in the calculation of the extremes.

There is no obstacle for extending the application of the described procedure to cases where more complex F or φ functions have to be employed, or to non-isothermal kinetic functions. The application of the procedure is not even limited on solid-state kinetic functions; it can also be used in the analysis of other types of processes.

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Appendix A

The basic function

$$\Phi = t^m F$$

in differential form reads as

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = mt^{m-1}F + t^m F' = 0$$

which gives

$$t^{m-1}(mF + tF') = 0$$

or for $t > 0$

$$mF + tF' = 0$$

and finally

$$mF(t_p(m)) = -t_p(m)F'(t_p(m))$$

Appendix B

Šestak and Bergren [20] proposed an empirical kinetic model in the form:

$$f(\alpha) = \alpha^r(1-\alpha)^p[-\ln(1-\alpha)]^q$$

after eliminating the first exponential term [21]

$$F = (1-\alpha)^p[-\ln(1-\alpha)]^q$$

Appendix C

The basic function

$$\Phi = \alpha^m H_1^p(\alpha) H_2^q(\alpha)$$

in differential form reads as

$$\frac{\mathrm{d}\Phi}{\mathrm{d}\alpha} = m\alpha^{m-1} H_1^p(\alpha) H_2^q(\alpha) + \alpha^m p H_1^{p-1}(\alpha) H_1'(\alpha) H_2^q(\alpha) + \alpha^m H_1^p(\alpha) q H_2^{q-1}(\alpha) H_2'(\alpha) = 0$$

or

$$\frac{\mathrm{d}\Phi}{\mathrm{d}\alpha} = \alpha^{m-1} H_1^{p-1}(\alpha) H_2^{q-1}(\alpha)[m H_1(\alpha) H_2(\alpha) + \alpha p H_1'(\alpha) H_2(\alpha) + \alpha q H_1(\alpha) H_2'(\alpha)] = 0$$

which gives

$$m H_1(\alpha) H_2(\alpha) = -p[\alpha H_1'(\alpha) H_2(\alpha)] - q[\alpha H_1(\alpha) H_2'(\alpha)]$$

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