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THE SINGLE-STEP APPROXIMATION
Attributes, strong and weak sides

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Mechanisms of the processes in condensed phase tend to occur in multiple steps that have different rates. Their kinetics is very often described by the single-step approximation. The first attribute of the approximation is the substitution of a generally complex set of kinetic equations describing the complex process by the sole single-step kinetic equation. The other attributes of the approximation are the separability of the temperature and conversion functions and the additivity. The temperature function for the best fit of experimental data may not be the Arrhenius relationship. The main strength of the single-step approximation is that it enables a mathematical description of the kinetics of solid-state reactions without a deeper insight into their mechanism. The low trustworthiness of far extrapolation is a weak point.

Keywords: *additivity, condensed phase, function separability, kinetics, modeling, single-step approximation*

Introduction

Processes in condensed phase are extensively studied by thermoanalytical methods. Mechanisms of these processes are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, the methods based on the single-step approximation are often used, either the model-free or model-fitting ones.

In the previous paper [1], fundamentals of the isoconversional methods based on the Arrhenius expression of the temperature function have been summarised. The physical meaning of the activation parameters has been analysed and it was concluded that the parameters are apparent quantities, in general without a mechanistic interpretation. In paper [2] the idea of single-step approximation has been introduced and application of non-Arrhenius temperature functions has been justified. It has been demonstrated that the use of these functions removes the problems with calculation of the temperature integral. In the very latest paper of this series [3] it has been reasoned that the main contribution of the single-step approximation is that it enables a mathematical description of the kinetics of solid-state reactions without an insight into their mechanism. In this paper the main attributes, strengths and weaknesses of the single-step approximation are identified and analyzed.

Attributes of the single-step approximation

Complex mechanisms and the single-step approximation

It is generally recognized that the rate of the processes in condensed state is a function of temperature and conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(T,\alpha) \qquad (1)$$

The single-step kinetics approximation employs the assumption that the function Φ in Eq. (1) can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on the temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α:

$$\Phi(T,\alpha) = k(T)f(\alpha) \qquad (2)$$

Combining Eqs (1) and (2), the rate of the complex multi-step condensed-state process can be formally described as [1]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \qquad (3)$$

Equation (3) is mostly called the general rate equation. It resembles a single-step kinetic equation, even though it is a representation of the kinetics of a complex condensed-phase process. The single-step approximation thus resides in substituting a generally complex set of kinetic equations by the sole sin-

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gle-step kinetic equation. This is the first attribute of the single-step approximation.

The temperature function in Eq. (3) is mostly considered to be the rate constant and the conversion function is considered to reflect the mechanism of the process. It was discussed in [2] that this interpretation of the both functions may be incorrect. Since Eq. (3) is a mathematical formulation of the single-step approximation, the functions $k(T)$ and $f(\alpha)$ represent, in general, just the temperature and conversion components of the kinetic hypersurface. The kinetic hypersurface is a dependence of conversion as a function of time and temperature [2].

With only for few exceptions, the temperature function is expressed by the Arrhenius equation

$$k(T) = A\exp\left[-\frac{E}{RT}\right] \tag{4}$$

where A and E are considered the preexponential factor and the activation energy, respectively, T is the absolute temperature and R stands for the gas constant. In [2, 3] it has been justified that, since $k(T)$ is not the rate constant, there is no reason to be confined to the Arrhenius relationship and use of two non-Arrhenius temperature functions was suggested:

$$k(T) = AT^{\mathrm{m}} \tag{5}$$

$$k(T) = A\mathrm{e}^{\mathrm{DT}} \tag{6}$$

where m and D are parameters. A great advantage of the application of Eqs (5) and (6) is that, in contrary to Eq. (4), the temperature integral can be expressed in a closed form [2]. Unlike the temperature functions, there is a wide range of conversion functions applied. Practically every function is connected with a certain idea of reaction mechanism [2, 3].

Imperative of the function separability

The importance of function separability in the single-step approximation has been first pointed out in [2] and analyzed more in detail in [3]. Especially for the isoconversional methods it is generally recognised that they lead to the dependence of adjustable parameters in the temperature function on conversion. For example, when solving Eq. (3) using the Arrhenius temperature function, E is considered to be constant. Subsequently, after the separation of variables and integration, one can obtain the result:

$$\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = A\int_0^{t_\alpha}\exp\left[-\frac{E}{RT}\right]\mathrm{d}t \tag{7}$$

If E is a function of conversion, A also varies with conversion. Equation (3) then can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(\alpha)\exp\left[-\frac{E(\alpha)}{RT}\right]f(\alpha) \tag{8}$$

where $A(\alpha)$ and $E(\alpha)$ are the parameters A and E depending on the conversion. Equation (7) thus does not represent the formal solution of Eq. (3) since the variables are not separated (A and E are functions of conversion). From the variations of activation energy quite often the conclusions are drawn on the change of the reaction mechanism. This would mean that the conversion function is also a function of temperature so that Eq. (3) would take the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(\alpha)\exp\left[-\frac{E(\alpha)}{RT}\right]f(\alpha, T) \tag{9}$$

Equation (9) emphasizes even more strongly that Eq. (7) does not represent the formal solution of Eq. (3). Hence, in the case of variable activation energy the basic assumption of the single-step approximation (i.e., the separability of the both functions) is violated and the description of the experimental kinetic data is inadequate. The concept of variable activation energy thus appears mathematically incorrect and inherently self-inconsistent. Deductions drawn from the dependence of activation energy on conversion can hardly be considered trustworthy and should be judged very critically and carefully. The same conclusion on the inseparability of the temperature and conversion functions has been made in [2] for the case of parameters m and D in Eqs (5) and (6) depending on conversion.

For the application of single-step approximation, a couple of separable functions with constant parameters should be found. The separability of temperature and conversion functions means that the values of adjustable parameters should be unvarying in the whole range of conversions and temperatures. This is the second attribute of the approximation. Variable parameters indicate that the choice of either the temperature function or the conversion function is inappropriate.

Additivity

Separation of variables in Eq. (3) leads to the result

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = k(T)\mathrm{d}t \tag{10}$$

Temperature is generally a function of time. The existence of additivity in the single-step approximation is best illustrated using the two temperature regimes composed of two isothermal parts as shown in Fig. 1a. In the regime (A) the sample is heat-stressed at temperature T_1 for time t_s and subsequently at a higher temperature for the same time. In the regime (B), the order of temperatures is swapped. Inte-

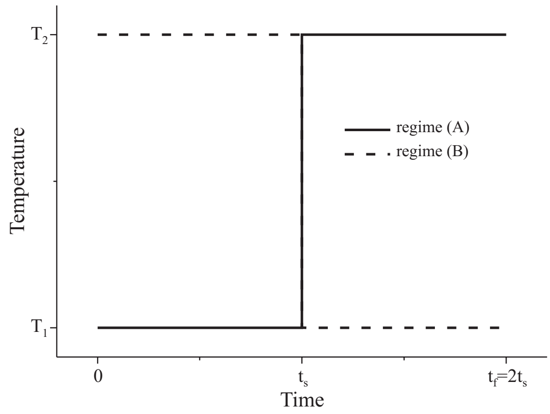

Fig. 1a The temperature regimes for the demonstration of additivity

gration of Eq. (10) for the first part of the temperature regime (A), i.e. for the time interval $<0;t_s>$, gives

$$F(\alpha_s,T_1)-F(0)=k(T_1)t_s \tag{11}$$

where $F(\alpha)$ is a primitive function of $1/f(\alpha)$ and $F(\alpha_s,T_1)$ is the value of the function F at temperature T_1 and time t_s. Integration for the second part, i.e. for the time interval $<t_s;t_f=2t_s>$, gives

$$F(\alpha_f)-F(\alpha_s,T_1)=k(T_2)t_s \tag{12}$$

The overall result of integration of Eq. (10) over the temperature regime (A) is obtained as a sum of Eqs (11) and (12):

$$F(\alpha_f)-F(0)=k(T_1)t_s+k(T_2)t_s \tag{13}$$

It can be very simply shown that the integration of Eq. (10) over the temperature regime (B) leads to the same overall result as Eq. (13). The situation is demonstrated in Fig. 1b where it can be seen that, although the integration paths for the both temperature regimes are different, the final result is the same. Hence, within the single-step approximation the effect of individual heat stresses can be expressed as a sum of corresponding increments of the function F. The overall effect is the same irrespective of the order of the heat stresses. It can be theoretically deduced that this additivity takes place if and only if Eq. (1) can be written in the factorized form of Eq. (3) [4]. A kinetic differential equation in the form of Eq. (3) is thus said to be additive whereas the kinetic equation in the form of Eq. (1) is called semi-additive [4–6]. The additivity rule can be generalized also for the prediction of the effects of other variables besides temperature on the rate of nonisothermal transformations [7].

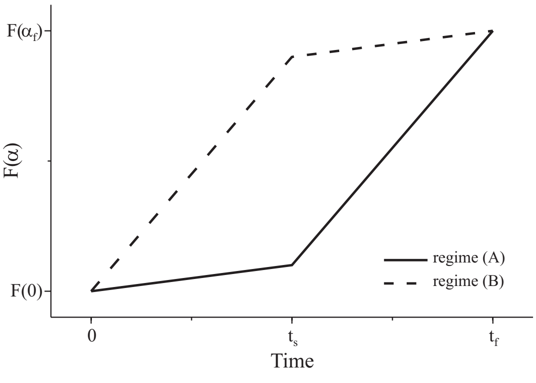

Fig. 1b Additivity of the function F corresponding to the temperature regimes shown in Fig. 1a

In the field of material stability, the additivity of the effects of various ageing stresses has led us to the concept of depleted and residual stability [8, 9] and to the determination of the equivalence of various ageing methods [10, 11].

Description of complex processes by the single-step approximation

When using thermoanalytical methods, we observe changes of aggregate physical properties, i.e. enthalpy and mass in the case of DSC, DTA and TG. In chemical kinetics, the conversion of the component A is defined as

$$\alpha_A=\frac{n_{A_i}-n_A}{n_{A_i}} \tag{14}$$

where n_{A_i} and n_A are the initial and actual moles of the compound A. In thermal analysis, the definition of conversion is

$$\alpha=\frac{X_{\mathrm{part}}}{X_{\mathrm{tot}}} \tag{15}$$

where X_{part} and X_{tot} are either the aggregate reaction enthalpy or the mass loss corresponding to the actual time (or temperature for nonisothermal processes) and to the end of the process. In the description of the kinetics studied by thermoanalytical methods it is necessary to distinguish between the two definitions of the conversion. This analysis is limited to the simplest case of the first-order reaction steps and constant volume of the reacting system. The first-order steps of the process are assumed to be elementary reactions where the temperature dependence of their rate constants obeys the Arrhenius relationship.

Reversible reactions

In this case the reaction scheme is

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \tag{16}$$

Provided that the reacting system is composed only of the compound A at the beginning of experiment, it can be very easily derived that the reaction rate can be expressed as

$$\frac{\mathrm{d}\alpha_{\mathrm{A}}}{\mathrm{d}t}=k_1[1-(1+K)\alpha_{\mathrm{A}}] \qquad (17)$$

where K is the equilibrium constant of the reaction (16). At the end of the process, the reaction rate equals zero so that the final conversion of the compound A, is

$$\alpha_{\mathrm{A_f}}=\frac{1}{1+K_{\mathrm{f}}} \qquad (18)$$

If the process is isothermal then K_{f}=K. In the case of a nonisothermal process (with increasing temperature) K_{f} is the equilibrium constant at the final temperature.

If the change in α_{A} is proportional to the change of properties measured by thermoanalytical instrument and taking into account Eq. (15), the 'thermoanalytical' conversion is expressed as

$$\alpha=\frac{\alpha_{\mathrm{A}}}{\alpha_{\mathrm{A_f}}} \qquad (19)$$

Combining Eqs (17)–(19), the reaction rate in the case of reversible reactions determined by thermal analysis is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1(1+K_{\mathrm{f}})[1-(1+K)\alpha] \qquad (20)$$

This equation can be separated and solved in the case of an isothermal process. For a nonisothermal process, the equilibrium constant K depends on temperature and Eq. (20) cannot be expressed in the factorized form of Eq. (3).

Parallel reactions

The reaction scheme in this case is

$$\begin{gathered}\mathrm{A}\xrightarrow{k_1}\mathrm{B}\\ \mathrm{A}\xrightarrow{k_2}\mathrm{C}\end{gathered} \qquad (21)$$

The kinetic equation can be written as

$$\frac{\mathrm{d}\alpha_{A}}{\mathrm{d}t}=(k_1+k_2)(1-\alpha_{\mathrm{A}}) \qquad (22)$$

At any instant, the products are formed in the ratio of the rate constants. Thus, the thermoanalytical conversion is expressed as

$$\alpha=\frac{1}{X_{\mathrm{tot}}}\int_0^{\alpha_{\mathrm{A}}}\left(\frac{k_1}{k_1+k_2}X_1+\frac{k_2}{k_1+k_2}X_2\right)\mathrm{d}\alpha_{\mathrm{A}} \qquad (23)$$

where X_1 and X_2 are the changes in the reaction enthalpy or mass corresponding to the first and the second step of the process (21). It is a matter of course that the total change is given as

$$X_{\mathrm{tot}}=\int_0^1\frac{k_1X_1+k_2X_2}{k_1+k_2}\mathrm{d}\alpha_{\mathrm{A}} \qquad (24)$$

Taking into account Eqs (23) and (24), from Eq. (22) one can get the 'thermoanalytical' rate equation:

$$\begin{gathered}\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{1}{X_{\mathrm{tot}}}(k_1X_1+k_2X_2)\cdot\\ \left(1-X_{\mathrm{tot}}\int_0^{\alpha}\frac{k_1+k_2}{k_1X_1+k_2X_2}\mathrm{d}\alpha\right)\end{gathered} \qquad (25)$$

For an isothermal process, the rate constants are constant and Eq. (25) degenerates into

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2)(1-\alpha) \qquad (26)$$

Comparing Eqs (22) and (26) it can be seen that for an isothermal process the 'kinetic' and 'thermoanalytical' conversions are identical. For a nonisothermal process, the rate constants depend on temperature and, consequently, the thermoanalytical rate equation given by Eq. (25) cannot be in general expressed in the factorized form of Eq. (3).

If the temperature range is not too wide or if the temperature dependence of the rate constants is not very steep, the ratio of the rate constants in the integral at the right-hand side of Eq. (25) can be considered constant and Eq. (25) obtains the form of Eq. (26) also for this case. The sum of the rate constants gives the effective rate constant of the aggregate process measured by thermal analysis:

$$k=k_1+k_2 \qquad (27)$$

As mentioned above, the rate constants of the elementary first-order reaction steps are considered to obey the Arrhenius relationship. The question is which relationship should be used for the temperature dependence of the effective rate constant. The quality of the fit of the effective rate constant by using Eqs (4)–(6) for various combinations of the Arrhenius parameters related to the rate constants of both elementary steps is given in Table 1. The fit is carried out by the linear least-squares method for the linearized forms of Eqs (4)–(6). It is considered that the higher is the absolute value of the correlation coefficient, the better is the fit. The best fit is marked by two asterisks and the satisfactory one by one asterisk. From Table 1 it can be seen that, despite the two elementary steps obey the Arrhenius equation, the Arrhenius equation represents the worst choice for the description of the temperature dependence of the effective rate constant.

Table 1 Fit of the temperature dependence of the effective rate constant given by Eq. (27) where k_1 and k_2 obey the Arrhenius relationship. Kinetic parameters related to k_1 are $A_1=1\cdot10^{13}$ min^{-1}, $E_1=120$ kJ mol^{-1} and those related to k_2 are: a – $A_2=1\cdot10^8$ min^{-1}, $E_2=80$ kJ mol^{-1}; b – $A_2=1\cdot10^4$ min^{-1}, $E_2=40$ kJ mol^{-1}; c – $A_2=0.1$ min^{-1}, $E_1=0$ kJ mol^{-1}. The fit is carried out for the temperature range 50–250°C using the linearized forms of Eqs (4)–(6). The linear dependence is expressed as $y=ax+b$

Combination	Eq.	*a*	*b*	Correlation coefficient
	(4)	24.38±0.40	–11698±163	–0.99815*
(a)	(5)	–176.42±0.24	28.583±0.040	0.99998**
	(6)	–32.79±0.47	0.0684±0.0011	0.99758
	(4)	13.92±0.71	–6530±291	–0.98161
(b)	(5)	–98.95±2.96	16.08±0.49	0.99129*
	(6)	–18.26±0.29	0.03879±0.00068	0.99706**
	(4)	7.05±1.43	–3419±585	–0.80146
(c)	(5)	–53.77±7.89	8.71±1.31	0.83679*
	(6)	–1.60±0.21	0.00438±0.00050	0.89537**

*Satisfactory fit, **best fit

Consecutive reactions

The reaction scheme in this case is

$$A\xrightarrow{k_1}B\xrightarrow{k_2}C \qquad (28)$$

The kinetics of consecutive reactions attracts attention of thermoanalysts for long time as documented in [12] and in the references cited therein. Ozawa treated the general case of the nonisothermal consecutive reactions [12]; it is needless to repeat his procedure. Two reduced times were involved in the solution of the nonisothermal equation so that the consecutive reactions were a system of multiple dimensions of time and the relation between them was dependent on the temperature regime. The main result regarding the topic of this paper is that the rate equation describing the kinetics of the consecutive reactions cannot be in general expressed in the factorized form of Eq. (3).

Strengths and weaknesses of the single-step approximation

Use of the single-step approximation for the complex processes

The parameters in Eqs (20) and (25) have a clear physical meaning. However, as shown in the previous section, for a complex process the equation describing the reaction rate cannot be factorized in the form of Eq. (3). It is necessary to underline that only the simplest cases of the complex processes have been investigated involving just two elementary first-order reaction steps as shown in the reaction schemes (16), (21) and (28). It is a matter of course that the existence of factorization can hardly be expected for more complex reaction schemes.

The impossibility to find a couple of separable functions $k(T)$ and $f(\alpha)$ with the parameters possessing a physical meaning does not mean that the single-step approximation could not be used for the description of thermoanalytical kinetic data. Mostly it is possible to find a couple of the separable temperature and conversion functions satisfactorily describing the experimental kinetic data. As discussed in [3], Eq. (3) is not a true kinetic equation in this case. It is just an empirical equation enabling to describe the experimental data and the parameters occurring in the temperature and conversion functions have no physical meaning. Regarding the choice of the functions, any couple of the functions leading to a satisfactory description of the experimental data, is suitable to be employed. This approach enables to reproduce the values of reaction rate, conversion, temperature and time observed experimentally. Also, the interpolation of the results should be trustworthy, i.e. the reaction rates, conversions, temperatures and times can be reliably estimated within the range of the measured data. Once the kinetic description is carried out, modeling of the kinetics of the process is feasible without a deeper insight into its mechanism [1]. This can be considered the strongest side of the single-step approximation.

Thermoanalytical techniques (DSC, TG) provide an aggregate, overlapped signal of all reaction steps occurring in the sample. It is indicated for example by Eq. (25) that, for the same process and time-temperature regime, the values of conversions and reaction rates obtained by various thermoanalytical methods may be different [2]. Hence, in the kinetic description of DSC experimental data, analysis of the rate and quantity of heat released/absorbed is done. Analogously, in the kinetic description of TG data, rate and quantity of mass loss is analysed [2].

Equation (3) can become the true kinetic equation in the following particular cases: (*i*) the process involves just one elementary step, (*ii*) a sole rate-limiting step exists in the process; (*iii*) only one step of the multi-step process is detected by the thermoanalytical technique (for example, when using TG for the study of the process involving two consecutive steps - isomerization and decomposition). In these cases, $k(T)$ would likely obey the Arrhenius relationship and $f(\alpha)$ would be closely connected with the reaction mechanism. However, one never can be sure that he deals with this case. No mechanistic conclusions based only on the thermoanalytical kinetic measurements should be drawn. For mechanistic considerations, additional supporting information from other methods is inevitable.

It can be summarized that, in general, Eq. (3) is the mathematical formulation of the single-step approximation and the functions $k(T)$ and $f(\alpha)$ represent the temperature and conversion components of the kinetic hypersurface. The adjustable parameters occurring in the both functions have no obvious physical meaning and they can vary with the range of experimental data so that the extrapolation of the results measured too far outside the experimental range cannot be considered trustworthy. The impossibility of far-reaching extrapolation is a weakness of the single-step approximation.

Recommendations

Since the parameters in the temperature and conversion functions have generally no physical meaning, it cannot be considered trustworthy to draw any conclusions just from their values (for example, it is not trustworthy to draw conclusions just from the values of activation energies). For drawing the conclusions, the physical properties accessible to measurement, i.e. the reaction rate, conversion, temperature and time, should be calculated using the parameters. Also, use of the relative criteria, such as the protection factor or the residual stability [9], should be preferred. Both criteria are given as ratios of isoconversional times. The temperature dependence of these criteria is much less steeper compared to the dependences of isoconversional times. The extrapolation of the criteria outside the region of the measurements is thus less risky.

When applying the single-step approximation, one has to bear in mind that it is just an approximation. The only essential requirement for the functions $k(T)$ and $f(\alpha)$ is that they have to be separable. The function separability is implicitly involved also in other kinetic considerations, for example in the concept of reduced time introduced by Ozawa [13]. If a couple of separable functions cannot be found, it indicates that the single-step approximation is too crude and another approach should be chosen for processing the experimental data [3]. Dependence of the adjustable parameters on α or T indicates an ill choice of the temperature or conversion function.

It is a frequently encountered opinion that a single non-isothermal experiment provides information on both $k(T)$ and $f(\alpha)$. A kinetic curve represents a projection of the time-temperature line to the kinetic hypersurface [2]. In order to completely map the hypersurface, a single kinetic curve is not sufficient, a set of curves is necessary covering entire part of the hypersurface of our interest. A single kinetic curve represents only a very limited part of the kinetic hypersurface and, therefore, the methods based on the processing just a single curve should be obviated.

Conclusions

Processes in condensed phase tend to occur in multiple steps that have different rates. The first attribute of the single-step kinetics approximation is the substitution of a generally complex set of kinetic equations describing the complex process by the sole single-step kinetics equation. The second attribute is the separability of the temperature and conversion functions. A plausible kinetic description should provide unvarying values of adjustable parameters both for temperature and conversion functions over the whole range of experimental data. The third attribute is the additivity of the primitive function of $1/f(\alpha)$.

The main strength of the single-step kinetics approximation is that it enables a mathematical description of the kinetics of solid-state reactions. The correct mathematical description should recover the values of conversion and the rate of the reaction under study for a given couple of time and temperature. In general, the functions $k(T)$ and $f(\alpha)$ represent the temperature and conversion components of the kinetic hypersurface so that the adjustable parameters occurring in the both functions have no obvious physical meaning. They may vary with the range of experimental data so that the extrapolation of the results measured too far outside the experimental range cannot be considered trustworthy. The impossibility of far-reaching extrapolation is a weakness of the single-step approximation. The temperature function for the best description of experimental data may not be the Arrhenius relationship.

When applying the single-step kinetics approximation, one has to bear in mind that it is just an approximation. It is a very useful tool for the description of the kinetics of processes studied by thermoanalytical methods. For its correct application, it is necessary to recognize its attributes, strong and weak sides.

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