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CONSIDERATIONS ON THE SINGLE-STEP KINETICS APPROXIMATION

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Mechanism of the processes in condensed phase 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 single-step kinetics approximation is often applied which resides in substituting a generally complex set of kinetic equations by the sole single-step kinetics equation. The main contribution of the single-step kinetics approximation is that it enables a mathematical description of the kinetics of solid-state reactions without a deeper insight into their mechanism. The single-step kinetics approximation is based on the assumption that the temperature and conversion functions are separable. In the paper, some consequences originating from ignoring the function separability are discussed.

Keywords: *activation energy, condensed phase, function separability, kinetics, modeling*

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 a single-step approximation are often used, either the model-free or model-fitting ones.

In a 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. The idea of single-step kinetics approximation has been introduced in paper [2]. The single-step kinetics approximation involves the imperative condition of the separability of both temperature and conversion functions. It has been reasoned that if a couple of separable functions cannot be found, it indicates that the single-step kinetics approximation is too crude and the description of the kinetic hypersurface is incorrect. 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. The kinetic hypersurface is a dependence of conversion as a function of time and temperature. In paper [2], 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 last years, intense discussions have been kept on the physical meaning of activation parameters obtained from thermoanalytical kinetic studies [3–6] or even the solidity of foundations of thermoanalytical kinetics has been appraised [7]. In this paper I would like to present my view on the problem. This paper represents a summary and generalization of my previous two papers [1, 2] and my discussions with a number of thermoanalysts.

Single-step kinetics approximation

Rate of the processes in condensed state is generally a function of temperature and conversion:

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

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:

$$\Phi(T,\alpha)=k(T)f(\alpha) \tag{2}$$

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

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

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

Discussion

Why to introduce the concept of single-step kinetics approximation

On the first view, there is nothing new in Eqs (1)–(3). Equation (3) has been employed in the kinetics of solid state processes for hundred years [3]. The reason why it is necessary to introduce the concept of single-step kinetics approximation, resides in the interpretation of Eq. (3).

Solid state reactions ordinarily demonstrate a tangled interplay of various chemical and physical processes such as solid state decomposition, reaction of gases with solids, phase transitions, diffusion, adsorption, desorption, etc. [9]. It is very rarely, if not never, a single-step process. Full and exact kinetic description of such a complex process would be very difficult or even impossible since a detailed mechanism of the process, or parameters occurring in related kinetic equations, could be unknown.

Equation (1) represents the mathematical formulation of general experience that the rate of the processes in condensed state is a function of temperature and conversion. For the description of the kinetics of a generally very complex solid-state reaction, Eq. (3) is used which is in fact a single step kinetics equation. Thus, my understanding of the problem is that Eq. (3) is not the general rate equation, as it is mostly interpreted. Equation (3) represents a mathematical formulation of the single-step kinetics approximation, which is an attempt to describe the kinetic hypersurface in a simple way irrespective of the complexity of the overall process. The word ‘approximation’ is the most important in order to make clear and stress that it is not a true kinetic equation. In general, Eq. (3) may not be straightforwardly connected with the reaction mechanism.

Temperature and conversion functions

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 is wrong. Since Eq. (3) is a 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.

Obviously due to the prevailing interpretation of $k(T)$ as the rate constant, apart from very few exceptions [2, 8, 9] it is universally postulated that the temperature function is expressed by the Arrhenius equation

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

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 Ref. [2] 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:

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

$$k(T)=Ae^{\mathrm{DT}} \quad (6)$$

Thermoanalytical community inclines to the Arrhenius relationship (4), which is, from the point of view of mathematical treatment, the most awkward one [2] since the temperature integral cannot be expressed in a closed form. A great advantage of the application of Eqs (5) and (6) is the removal of the problems with the calculation of temperature integral [2].

On the contrary to the universally accepted form of the temperature function, there is a wide range of conversion functions applied. Practically every function is connected with a certain idea of reaction mechanism. The conversion functions are reviewed, e.g., in [3]. However, as discussed above, Eq. (3) is not a true kinetic equation, it is just an approximation. Consequently, any couple of the separable functions $k(T)$ and $f(\alpha)$, leading to a satisfactory description of the kinetic data, is suitable to be employed. There is no reason to be restricted to Eqs (4)–(6) for the temperature function or to the forms of the conversion function reviewed in [3], other functions may be used as well.

Adjustable parameters

The temperature and conversion functions contain adjustable parameters. Their values are adjusted in the procedure of fitting in order to reach the best fit between the experimental data and the data calculated using Eq. (3). In order to obtain the values of parameters which enable trustworthy modeling of kinetics, non-linear least squares methods should be used for fitting [1, 2].

The physical meaning of the parameters A and E in Eq. (4) as the preexponential factor and activation energy is connected exclusively with the formation of activated complex in an elementary reaction step. This is evidently not the case in the description of kinetic behaviour of complex condensed-phase processes within the framework of single-step kinetics approximation. As discussed in [1], A and E are just adjustable parameters in the temperature function, in general having no obvious physical meaning. Their values are composite where the representation of individual subprocesses in the values of A and E can be obscure. Therefore, one should be very cautious when using them for mechanistic considerations. The parameters A and E in Eq. (4) are called the preexponential factor and activation energy probably just because of the force of habit; however, this terminology is very deceiving and it is noticeable throughout the papers published that A and E are mostly understood to be true activation parameters. I agree with the author of Ref. [4] who wrote: 'In some articles, the magnitude of activation energy reported appears to be the principal result, perhaps even the dominant motivation for the investigation. However, compelling reasons for such a preoccupation with the measurements of activation parameters are not usually provided.' The papers dealing with the determination of adjustable parameters A and E should, at least, outline an idea of their further employment.

The main assumption of the single-step kinetics approximation should be emphasised here again that the two functions are separable and independent of each other, $k(T)$ depending solely on temperature and $f(\alpha)$ depending solely on the conversion of the process. It means that the adjustable parameters occurring in temperature function should not depend on conversion and vice-versa. A plausible kinetic description should provide unvarying values of adjustable parameters both for temperature and conversion functions over the whole range of experimental data.

Isoconversional methods

In isoconversional methods, the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ in Eq. (3) is constant and the reaction rate is a function of temperature only. The isoconversional methods can be crudely divided into two groups, i.e., the isothermal methods and the methods at linear heating. The latter group can be further subdivided into differential, integral and incremental methods. These methods are reviewed in a number of papers, see for example [1, 2, 10] and the references cited therein. They are often called the model-free methods since the value of conversion function for the fixed value of conversion is implicitly involved in the adjustable parameter A_α [1, 2].

Regarding the isoconversional methods, it is generally recognised that they lead to the dependence of adjustable parameters in the temperature function on conversion. This fact has led to the concept of variable activation energy (see [3,10] and the references cited therein). As shown in [1], dependence of activation energy on conversion leads to the inseparability of Eq. (3). The latter statement leads to so serious consequences that I feel the need of reasoning it in more details.

When solving Eq. (3) under the assumption of validity of the Arrhenius equation, E is considered to be constant. Subsequently, after the separation of variables and integration, one can obtain the result:

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

If E is a function of conversion, Eq. (3) can be rewritten as

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

where $E(\alpha)$ is the parameter E depending on the conversion. Equation (7) thus does not represent the formal solution of Eq. (3) since the variables are not separated (E is a function of conversion).

The same conclusion on the inseparability of the temperature and conversion functions has been made in [2] for the parameters m and D in Eqs (5) and (6) depending on conversion. Thus, in the case of variable activation energy the basic assumption of the single-step kinetics approximation (i.e., the separability of the both functions) is violated and the description of the experimental kinetic data is inadequate. This represents the 'logical trap' of the concept of variable activation energy since it is 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.

Réti [11] tried to solve the problem with separability by introducing the relationship for the dependence of the activation energy on conversion:

$$E = E_0 + Th(\alpha) \qquad (9)$$

where E_0 is the activation energy at zero conversion and $h(\alpha)$ is a function of conversion. Combining Eqs (3), (4) and (9), one gets:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\exp\left[\frac{h(\alpha)}{R}\right]\exp\left[-\frac{E_0}{RT}\right] \tag{10}$$

Equation (10) contains a new conversion function, f_2:

$$f_2(\alpha) = f(\alpha)\exp\left[\frac{h(\alpha)}{R}\right] \tag{11}$$

Equation (10) is thus formally of the same form as the combination of Eqs (3) and (4) so that the problem of function separability replicates. Hence, Eq. (9) does not represent a way to eliminate the violation of the basic assumption of the single-step kinetics approximation.

The inseparability of the temperature and conversion factors is obviously among the most important factors bringing about the inconsistency in ‘activation parameters’ obtained from isothermal and non-isothermal isoconversional methods [1]. For the application of single-step kinetics approximation, a couple of separable functions has to be found. Since the value of conversion function for the given value of conversion is implicitly involved in the adjustable parameter A_α, there can be drawn the only conclusion: an inappropriate choice of the temperature function is responsible for the variability of activation energy (or better said, for the variability of adjustable parameter E).

Escape from the logical trap

If the temperature function is expressed by Eq. (5) or Eq. (6), the following relationships can be derived for the relationships between the adjustable parameters [2]:

$$E = mRT \tag{12}$$

$$E = RT^2 D \tag{13}$$

Thus, when applying Eq. (5)/Eq. (6), an implicit assumption of the linear/quadratic dependence of E on T is assumed. If the treatment of experimental data still leads to variable values of adjustable parameters, there is a possibility to postulate that the temperature function is equal to the sum of two partial functions, similarly as suggested by Flynn [12]:

$$k(T) = k_1(T) + k_2(T) \tag{14}$$

Equation (3) then obtains the form:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)[k_1(T) + k_2(T)] \tag{15}$$

If the partial temperature functions are expressed by Eqs (4), (5) or (6), following the procedure presented in [1, 2], for the isothermal isoconversional method one can obtain:

$$t_\alpha = \frac{1}{A_\alpha \exp\left[-\frac{E_1}{RT}\right]\left\{1 + \frac{A_2}{A_1}\exp\left[\frac{E_1 - E_2}{RT}\right]\right\}} \tag{16}$$

$$t_\alpha = \frac{1}{A_\alpha T^{m_1}\left[1 + \frac{A_2}{A_1}T^{m_2 - m_1}\right]} \tag{17}$$

$$t_\alpha = \frac{1}{A_\alpha e^{D_1 T}\left[1 + \frac{A_2}{A_1}e^{(D_2 - D_1)T}\right]} \tag{18}$$

where t_α is the time at which the conversion α is reached. The parameter A_α is given as:

$$A_\alpha = \frac{A_1}{F(\alpha) - F(0)} \tag{19}$$

where F is the primitive function of $1/f$. The subscript α at A_α designates the value related to the fixed value of conversion.

Analogously, for the isoconversional integral method at linear heating it can be derived:

$$\beta = A_\alpha \int_0^{T_\alpha} \left\{\exp\left[-\frac{E_1}{RT}\right] + \frac{A_2}{A_1}\exp\left[-\frac{E_2}{RT}\right]\right\}\mathrm{d}T \tag{20}$$

$$\beta = A_\alpha\left[\frac{T_\alpha^{m_1+1}}{m_1 + 1} + \frac{A_2}{A_1}\frac{T_\alpha^{m_2+1}}{m_2 + 1}\right] \tag{21}$$

$$\beta = A_\alpha\left[\frac{e^{D_1 T_\alpha} - 1}{D_1} + \frac{A_2}{A_1}\frac{e^{D_2 T_\alpha} - 1}{D_2}\right] \tag{22}$$

where β is the heating rate and T_α is the temperature at which the fixed conversion α is reached. The lower integration limit in Eqs (20)–(22) is set to T_0=0 K since no process occurs in the sample at the starting temperature of the experiment. The temperature integral at the right side of Eq. (20) has to be solved numerically or by an expansion into series as reviewed by Flynn [13].

Equation (14) takes into account that the temperature function may be more complex than those given by Eqs (4)–(6). I believe the use of this function could lead to unvarying values of adjustable parameters and, thus, the mathematical incorrectness could be removed. On the other hand, the beautiful simplicity of the single-step kinetics approach is retained. If the adjustable parameters are unvarying, no differential or incremental methods of obtaining the parameters are needed. In this case, the parameters obtained should be the same irrespectively of the method used to obtain them. Within an experimental error, the differential, incremental and integral isoconversional methods should give the same values of parameters. This removes the problems connected with differential methods where these employ instantaneous rate values and, consequently, they are very sensitive to experimental noise and tend to be numerically unstable.

The relationships between the adjustable parameters can be derived from Eq. (14). For the partial temperature functions expressed by Eqs (4), (5) or (6), temperature derivative of the logarithmic form of Eq. (14) gives:

$$E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2} \tag{23}$$

$$m = \frac{k_1 m_1 + k_2 m_2}{k_1 + k_2} \tag{24}$$

$$D = \frac{k_1 D_1 + k_2 D_2}{k_1 + k_2} \tag{25}$$

In Fig.1, the dependences of E on temperature are shown for several combinations of adjustable parameters E_1 and E_2. It can be seen that, generally, the dependences are S-shaped curves. It is impossible to compare the shape of the curves with published data since the published data are deformed by the mentioned mathematical incorrectness.

When treating the experimental data, one should first test the invariability of adjustable parameters for the isoconversional methods based on Eqs (4)–(6) [1, 2]. The temperature function given by Eq. (14) should be employed in the case when the parameters vary with conversion. For the isoconversional methods based on Eq. (14), the temperature function has four adjustable parameters. For their reliable determination, the data for 7 temperatures (for isothermal runs) or 7 scans (for linear heating) are needed at least. It means that it will be more laborious to obtain the experimental data comparing to the isoconversional methods based on Eqs (4)–(6), where the minimum required temperatures or scans is 5. In order to carry out complete mapping of kinetic hypersurface, the temperature region for isothermal measurements should be so wide as possible in order to obtain trustworthy values of the parameters. Analogously, for nonisothermal measurements the scans should include also very low values, such as 0.1 K min^{-1} or even less. Equations (16)–(18) and (20)–(22) cannot be linearized and the parameters have to be obtained by a non-linear regression method.

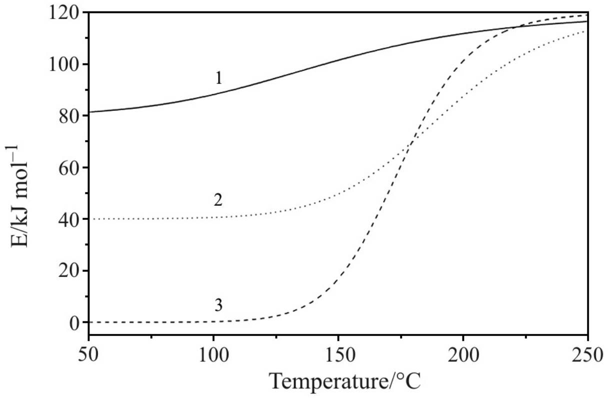

Fig. 1 Apparent parameter E calculated from Eq. (23) for the values: $A_1=1\cdot10^{13}$ min^{-1}, $E_1=120$ kJ mol^{-1} and (1) $A_2=1\cdot10^{8}$ min^{-1}, $E_2=80$ kJ mol^{-1}; (2) $A_2=1\cdot10^{4}$ min^{-1}, $E_2=40$ kJ mol^{-1}; (3) $A_2=0.1$ min^{-1}, $E_1=0$ kJ mol^{-1}

Method with explicit expression of the conversion function

It is traditionally expected that kinetic analysis produces an adequate kinetic description of the process in terms of the reaction model and Arrhenius parameters. These three components ($f(\alpha)$, E and $\ln A$) are sometimes called the 'kinetic triplet'. The most popular procedure is force fitting of experimental data to different reaction models. Henceforth, this procedure is referred to as the 'model-fitting method' [10].

In the model-fitting method, the Arrhenius relationship is used exclusively to describe the temperature dependence of the reaction rate. Mainly for the non-isothermal kinetic data, almost any $f(\alpha)$ can satisfactorily fit data at the cost of dramatic variations in the Arrhenius parameters, as it is nicely demonstrated in [10]. The reason is assumed to be in the fitting method where the parameters A and E and the reaction model $f(\alpha)$ are adjusted simultaneously. This extra flexibility in the fitting procedure allows errors in the functional form of the reaction model to be concealed by making compensating errors in the Arrhenius parameters [10]. Very often, a linear relation between ln A and the activation energy E is observed:

$$\ln A = a + bE \tag{26}$$

where a and b are constants. The relationship (26) is called the compensation effect (see [7, 14, 15] and the references therein).

I suspect that the choice of a couple of inseparable temperature and conversion functions could be responsible both for the variations in the activation parameters with the conversion function and the compensation effect. In principle, model-free and model-fitting methods should give the same values of adjustable parameters (within the experimental errors). The importance of function separability is emphasised above for the isoconversional methods. If the model-free treatment of kinetic data would lead to the variable activation energy, there is no reason to assume that the model-fitting treatment of the same data would give a sole unambiguous value of activation energy. Neither for the model-fitting treatment it is necessary to be tied to the Arrhenius relationship, the temperature functions (5), (6) or (14) can be used as well. One has just to be sure to deal with a couple of separable functions.

It is a widespread 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. 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 so my opinion is that the methods based on the processing just a single curve should be obviated.

NPK method

The non-parametric kinetics method (NPK), developed a few years ago [16–18], represents a special approach for processing the kinetic data. The method introduces a new point of view in kinetic analysis. It is also based on the single-step kinetics approximation, so that the basic relationship for the analysis of kinetic data represents Eq. (3). The experimental values of reaction rates are arranged in a matrix which is expressed as a product of two vectors containing information on $k(T)$ and $f(\alpha)$. The vectors are decoupled by matrix manipulations. The most important feature of the method is that it enables to decouple the vectors related to the temperature and conversion functions without the need of any assumptions about their functionality.

The two vectors containing information on $k(T)$ and $f(\alpha)$ are linearly independent which means that the discrete points forming the vectors originate in two separable functions. Validity of Eq. (3) is the only assumption made in the development of NPK. This method thus can be used as a testing method for the methods using analytical forms of $k(T)$ and $f(\alpha)$, i.e., the model-free and model-fitting methods. For a textbook case of the first-order kinetics, i.e., for the decomposition of organic peroxides it can be seen [16–18] that the vector carrying the information on temperature function resembles the Arrhenius relationship and the conversion function is unequivocally first-order. For a more complicated case of the methyl methacrylate polymerisation [18], the temperature vector does not resemble the Arrhenius dependence at all, it even exhibits a hump. The conversion function is also pretty complex, not corresponding to any of the models used for the model-fitting treatment.

NPK is a perfect method for the description of kinetic data. It is quite surprising that it is not applied more extensely. A probable reason is that, on the first sight, it looks quite laborious and I guess it could be automated with difficulties.

Conclusions

The main contribution 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. Thermoanalytical techniques (DSC, TG) provide a global, overlapped signal of all subprocesses occurring in the sample. 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]. Once the kinetic description is carried out, modeling of the kinetics of the process is feasible without a deeper insight into its mechanism [1].

When applying the single-step kinetics approximation, one has to bear in mind that it is just an approximation. For a particular case of a single-step process or of a process with the sole limiting step, Eq. (3) can become the true kinetic equation of the process. In such a case, $k(T)$ would likely obey the Arrhenius relationship and $f(\alpha)$ would be closely connected with the reaction mechanism. However, in any other case, Eq. (3) is the mathematical formulation of the single-step kinetics approximation and the functions $k(T)$ and $f(\alpha)$ represent the temperature and conversion components of the kinetic hypersurface. In general, the adjustable parameters occurring in the both functions have no obvious physical meaning. The function $k(T)$ may not be the Arrhenius relationship and $f(\alpha)$ may not be one of the functions listed in [10]. The only essential requirement for $k(T)$ 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 [19]. If a couple of separable functions cannot be found, according to my opinion it indicates that the single-step kinetics approximation is too crude and another, a more sophisticated approach should be chosen for processing the experimental data.

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