Application of the single-step approximation in chemical kinetics

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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 our previous paper [1], the idea of single-step approximation has been introduced and in [2] 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 paper [3] the main attributes, strengths and weaknesses of the single-step approximation have identified. In this contribution the consequences of the additivity in the single-step approximation are analyzed.

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:

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

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]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

Eq. (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 single-step kinetic equation.

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 [1-3] 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 [1]. 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 refs. [1-3] 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.

The function separability and additivity
The importance of function separability in the single-step approximation has been first pointed out in [1] and analyzed more in detail in [2,3]. In general, the separability of temperature and conversion functions takes place only if the values of adjustable parameters are unvarying in the whole range of conversions and temperatures. Variable parameters indicate that the choice of either the temperature function or the conversion function is inappropriate [3]. Separation of variables in Eq.(3) leads to the result

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = k(T)\mathrm{d}t \qquad (5)$$

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. Integration of Eq.(5) for the first part of the temperature regime (A), i.e. for the time interval $<0;t_s>$, gives

$$\mathrm{F}(\alpha_s, T_1) - \mathrm{F}(0) = k(T_1)t_s \qquad (6)$$

where $\mathrm{F}(\alpha)$ is a primitive function of $1/\mathrm{f}(\alpha)$ and $\mathrm{F}(\alpha_s, T_1)$ 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

$$\mathrm{F}(\alpha_f) - \mathrm{F}(\alpha_s, T_1) = k(T_2)t_s \qquad (7)$$

The overall result of integration of Eq.(5) over the temperature regime (A) is obtained as a sum of Eqs.(6) and (7):

$$\mathrm{F}(\alpha_f) - \mathrm{F}(0) = k(T_1)t_s + k(T_2)t_s \qquad (8)$$

It can be very simply shown that the integration of Eq.(5) over the temperature regime (B) leads to the same overall result as Eq.(8). 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 [3]. This is the most important consequence of the additivity in the single-step approximation. 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 [4,5] and to the determination of the equivalence of various ageing methods [6,7].

Use of the single-step approximation for complex processes
In [3] it has been proved that, in the case of a complex mechanism, the kinetic description of the process cannot be reduced to the simplified form of Eq.(3). However, the impossibility to find a couple of separable functions $k(T)$ and $\mathrm{f}(\alpha)$ with the parameters possessing a physical meaning does not mean that the single-step approximation could not be used for the description of 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 [2,3], Eq. (3) is not a true kinetic equation in this case. It is just an empirical equation enabling to describe the experimental data so that the consequence is that the parameters 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 [1-3]. This can be considered the strongest side of the single-step approximation. On the other hand, the missing physical meaning of the kinetic parameters brings about the impossibility of extrapolation far outside the measured temperature and conversion regions. This is a weakness of the single-step approximation.

Eq. (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.

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 with a clear physical meaning and 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 [5], 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. 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 [2]. Dependence of the adjustable parameters on α or T indicates an ill choice of the temperature or conversion function.

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[2] P.Šimon, J.Therm.Anal.Cal., 82 (2005) 651.
[3] P.Šimon, J.Therm.Anal.Cal., 88 (2007) 709.
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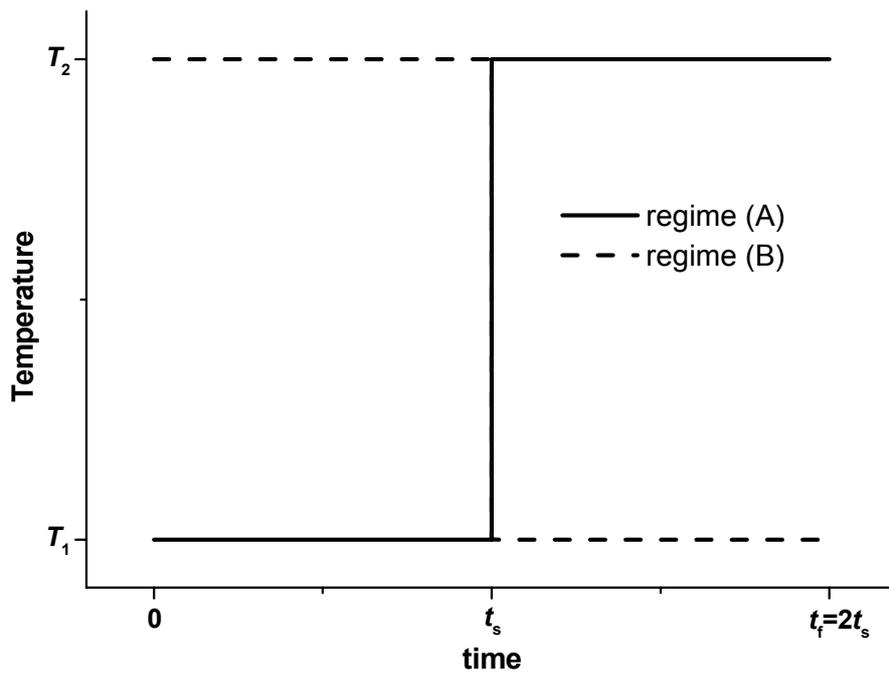[7] P.Šimon, M.Fratričová, P.Schwarzer and H.-W.Wilde, J.Therm.Anal.Cal., 84 (2006) 679.

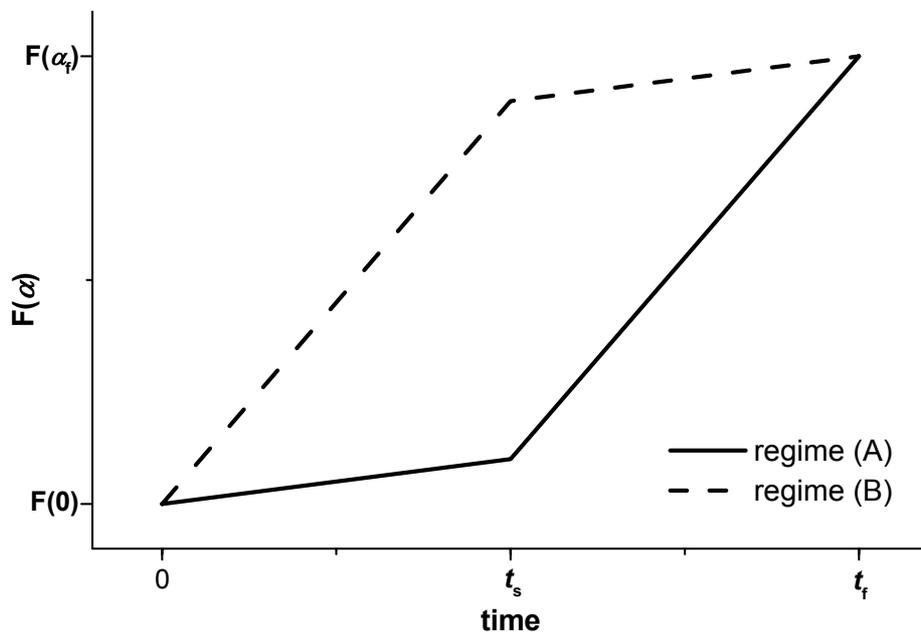**Fig.1a**. Temperature regimes for the demonstration of additivity.

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