

MODEL-FREE KINETICS

Staying free of multiplying entities without necessity*

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The paper presents the model-free kinetic approach in the context of the traditional kinetic description based on the kinetic triplet, A , E , and $f(\alpha)$ or $g(\alpha)$. A physical meaning and interpretability of the triplet are considered. It is argued that the experimental values of $f(\alpha)$ or $g(\alpha)$ and A are unlikely to be interpretable in the respective terms of the reaction mechanism and of the vibrational frequency of the activated complex. The traditional kinetic description needs these values for making kinetic predictions. Interpretations are most readily accomplished for the experimental value of E that generally is a function of the activation energies of the individual steps of a condensed phase process. Model-free kinetic analysis produces a dependence of E on α that is sufficient for accomplishing theoretical interpretations and kinetic predictions. Although model-free description does not need the values of A and $f(\alpha)$ or $g(\alpha)$, the methods of their estimating are discussed.

Keywords: activation energy, condensed phase, DSC, reaction kinetics, solids, thermogravimetry

Introduction

The kinetic analysis based on an isoconversional method is frequently referred to as ‘model-free’ because it allows the effective activation energy to be evaluated for different constant extents of conversion without assuming any particular form of the reaction model. By using an isoconversional method one does not obtain directly either the reaction model or pre-exponential factor, but the effective activation energy that tends to vary with the extent of conversion. The resulting kinetic description is sometimes seen as inadequate from the standpoint of the standard kinetic description that is usually based on a single constant set of the reaction model, pre-exponential factor, and the activation energy. In this paper, we argue that in the standard kinetic description the experimentally determined reaction model and preexponential factor are deficient in physical meaning and needed only for the practical purpose of kinetic predictions. However, the model-free approach allows kinetic predictions to be accomplished without evaluating the reaction model and pre-exponential factor that makes these two practically redundant.

Meaning and use of kinetic triplet

The rate of many condensed phase chemical reactions can be conveniently parameterized as a function of

the temperature, T , and the extent of the reactant conversion, α , as follows

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The conversion dependence is represented by a reaction model, $f(\alpha)$ that may take a large number of mathematical forms depending on the physical mechanism assumed in the mathematical derivations [1]. The temperature dependence is almost universally described by the Arrhenius equation so that Eq. (1) takes the form

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (2)$$

where A and E are Arrhenius parameters (the preexponential factor and the activation energy, respectively) and R is the gas constant. The kinetic triplet (i.e., A , E , and $f(\alpha)$) is the typical outcome of the regular kinetic analysis. What is the purpose of obtaining the kinetic triplet? There are two major purposes: one is theoretical, another is practical.

Theoretically, each of the kinetic triplet components represents an important physical concept. For instance, the transition state theory [2] links E to the energy barrier and A to the vibrational frequency of the activated complex. Numerous solid state reaction models [1] link $f(\alpha)$ to the reaction mechanism. Therefore, evaluating the kinetic triplet provides an

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opportunity of theoretically interpreting experimental data. However, it is used sometimes to simply satisfy the natural scholarly desire to speak the highbrow language when discussing dull experimental data (e.g., decomposition of municipal waste).

Practically, the kinetic triplet is needed to provide a mathematical description of the process. If the kinetic triplet determined correctly, it can be used to reproduce the original kinetics data as well as to predict the process kinetics outside the experimental temperature region. For example, by integrating and rearranging Eq. (1) one can derive Eq. (3)

$$t_{\alpha} = \frac{g(\alpha)}{A \exp\left(\frac{-E}{RT_0}\right)} \quad (3)$$

where $g(\alpha)$ is the integral form of the reaction model. Equation (3) allows one to predict at any desired temperature, T_0 , the time to reach any extent of conversion, t_{α} . Henceforth, the subscript α denotes the values related to a given extent of conversion. Equation (3) clearly demonstrates that an adequate mathematical description requires the complete triplet.

The question arises does the experimental kinetic triplet serve the aforementioned purposes? By experimental kinetic triplet we mean the values of E , A and $f(\alpha)$ or $g(\alpha)$ determined by fitting experimental kinetic curves to rate equations. Let us start from the practical purpose. In order to serve this purpose the experimental kinetic triplet should be sufficient for reproducing the original kinetic data and most importantly for correctly predicting the process kinetics outside the experimental temperature region. Although the casual evaluation of the kinetic triplet is an easy task, it is a challenge to determine the adequate kinetic triplet from experimental data. Most commonly, the kinetic triplet is determined by fitting a kinetic curve (α or $d\alpha/dt$ vs. T) obtained at a single heating rate to the rate equation in its differential Eq. (1) or integral form (e.g., Coats-Redfern equation [3]). This approach has been known to produce significantly differing kinetic triplets that, however, are capable of satisfactorily reproducing the original experimental data [4]. A spectacular example of this situation was given by Maciejewski [5] who demonstrated that at the heating rate $\beta = 5^{\circ}\text{C min}^{-1}$ the reaction order model, F_n : $(1-\alpha)^n$ with $n=0.673$, $E=147 \text{ kJ mol}^{-1}$ and $\ln A=11.451 \text{ s}^{-1}$ and the diffusion model, D_3 : $(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$ with $E=308 \text{ kJ mol}^{-1}$ and $\ln A=29.423 \text{ s}^{-1}$ describe exactly the same kinetic curve (Fig. 1).

Although the differing kinetic triplets may be capable of reproducing the original kinetic curves, they give rise to significantly different predictions [4] and, therefore, fail to serve any practical purpose. The flawed nature of the single heating rate kinetic meth-

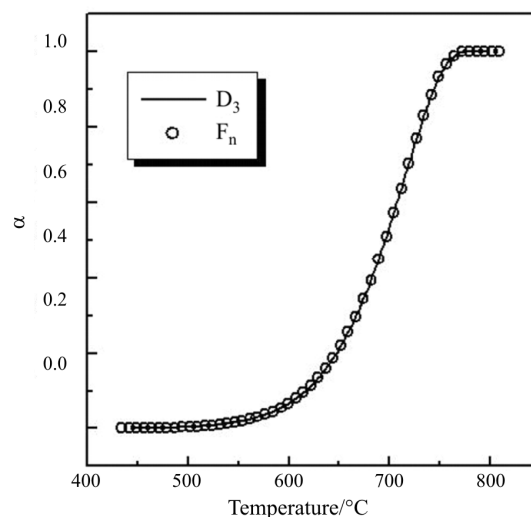


Fig. 1 Two different kinetic triplets (see text) correspond to the same kinetic curve

ods was stressed in discussions [5, 6] of the results of the ICTAC Kinetics Project [7], whose purpose was to compare various kinetic methods vs. the same sets of experimental and simulated data. The general recommendation of the Project was that for reliable kinetic evaluations one should use the methods that employ kinetic curves obtained at multiple heating rates, or, more generally, at multiple heating programs (e.g., several heating rates or/and temperatures). Unfortunately, similar recommendations are not typically found in the kinetic chapters of the monographs dealing with thermal analysis and thermal decomposition. The single and multiple heating rate methods are usually treated equally in the monographic literature that leaves the reader with a not-so-tough choice between spending either a few hours or a few days in the lab in order to accomplish seemingly identical kinetic results. However, only the methods using multiple heating programs are generally capable of producing kinetic triplets that can serve the practical purpose of predicting kinetic curves outside the experimental temperature range.

Does the experimental kinetic triplet serve the theoretical purpose? Can we interpret the respective values in terms of the energy barrier, the vibrational frequency, and the mechanism? Before answering this question we should stress that it makes sense only if the experimental kinetic triplet has been found adequate to the practical purposes of describing the experimental data and predicting kinetic curves outside the experimental temperature region. If the experimental kinetic triplet does not provide an adequate mathematical description, the question of its interpretability becomes irrelevant (e.g., how one can assign a physical meaning to the two different kinetic triplets describing the same process as shown in Fig. 1?).

Table 1 List of reaction models typically used in kinetic analyses

N	Reaction model	$f(\alpha)$	$g(\alpha)$
1	power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	one-dimensional diffusion	$1/2\alpha^{-1}$	α^2
6	Mampel (first order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami-Erofeev	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
10	three-dimensional diffusion	$2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
11	contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$

Assuming we have an adequate experimental kinetic triplet, let us consider the theoretical interpretability of its components. Can we interpret the best fit $f(\alpha)$ or $g(\alpha)$ as a reaction mechanism? This approach definitely looks like a very easy way to learn the reaction mechanisms, and has been frequently used for this purpose. Unfortunately, there is fundamental ambiguity [8] standing in the way of interpreting the best fit mathematical functions $f(\alpha)$ or $g(\alpha)$ as a reaction mechanism. Firstly, the $f(\alpha)$ or $g(\alpha)$ models are chosen from an unavoidably incomplete list of models such as that given in Table 1. No matter how many models are included in the tryout list, there is no guarantee that it includes the appropriate model

(maybe it is yet to be designed!). However, any list of the models will always produce some best-fit models. For instance, Fig. 2 shows that the contracting cylinder model appears to be the best-fit model for the thermal decomposition of NH_4NO_3 [9]. However if we do not include this model in our tryout list (Table 1), the power law model, $g(\alpha)=\alpha^{3/2}$ would be the best fit. Secondly, sometimes different reaction mechanisms give rise to the same mathematical function $f(\alpha)$ or $g(\alpha)$. For instance, a simple first-order reaction mechanism is described by $g(\alpha)=-\ln(1-\alpha)$ which is obtained via respective integration of $f(\alpha)=1-\alpha$. On the other hand, $g(\alpha)=-\ln(1-\alpha)$ is a special case of the Avrami-Erofeev model $g(\alpha)=[-\ln(1-\alpha)]^{1/n}$ that was derived assuming a rather complicated nucleation and growth mechanism [1]. In addition, some of the models have different mathematical forms but give rise to the kinetic curves that are very similar and may be difficult to resolve within an experimental error. The power law model, $g(\alpha)=\alpha^{3/2}$ and the contracting cylinder model, $g(\alpha)=1-(1-\alpha)^{1/2}$ provide an example of this situation (Fig. 2). It follows from the above that finding the best-fit mathematical model $f(\alpha)$ or $g(\alpha)$ is by no means sufficient for assigning the respective reaction mechanism to the process under consideration.

Can we theoretically interpret the experimental values of E and A in terms of the transition state theory concepts of the energy barrier and vibrational frequency? In order to find an answer to this question we need first to understand what we actually determine by fitting experimental rate data to theoretical rate equations. First of all, by using the thermal analysis methods (e.g., TG or DSC) we measure the overall process rate. The overall process is likely to involve multiple steps, and the existence of a single limiting step is rather an exception than a rule. The overall rate data are most commonly fit to a single step rate equa-

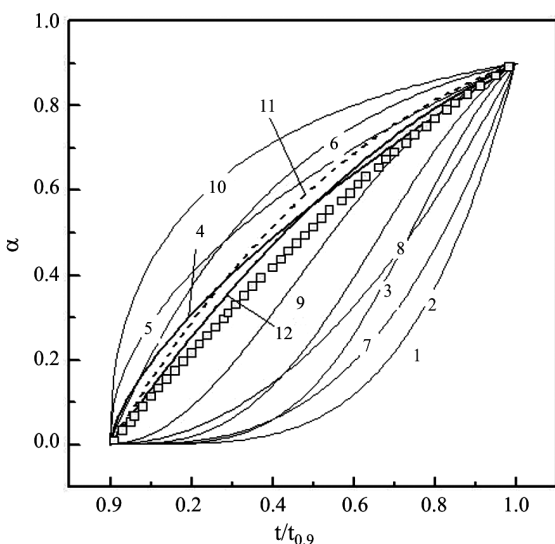


Fig. 2 Reduced time plots for different reaction models. Numbers by the curves correspond to the numbers in Table 1. Squares represent isothermal decomposition data of NH_4NO_3 averaged over three temperatures 156, 160, and 168°C

tion, or more rarely to a two-step equation. Assuming that the resulting kinetic triplet(s) provide an adequate mathematical description of the process (see above), what is the physical meaning of the best-fit E and A ? Their meaning is simple. The value of E is a temperature coefficient of the overall reaction rate. It is a value that shows how sensitive the overall reaction rate to the temperature variation. The value of A is a scaling factor of the overall reaction rate. It is a value of that characterizes the amplitude or the intensity of the overall reaction rate. Essentially, the experimental values of E and A do the same job as the activation enthalpy and the frequency factor in the transition state theory. However the theory in its classical formulation deals with the rate of a single chemical reaction that occurs in the absence of the reaction medium. In this circumstance, the rate depends on the height of the energy barrier that separates the reactants from the products and on the vibrational frequency of the activated complex.

The thermal analysis methods are applied to study the condensed phase reactions that occur in a solid or liquid medium. The presence of a medium adds a transport step to the chemical reaction step. As a result, the rate of conversion of the reactants into products becomes dependent on the chemical reaction rate as well as on the transport rate of the reactants and products in the reaction medium. In this case, the temperature dependence of the overall rate is described by the effective rate constant, k_{ef} as follows [10]

$$\frac{1}{k_{\text{ef}}} = \frac{1}{k_{\text{R}}} + \frac{1}{k_{\text{D}}} \quad (4)$$

where k_{R} and k_{D} are the reaction and diffusion rate constants respectively. Fitting the overall rate of such a process to a single step rate equation (Eq. 2) will yield the experimental value E that characterizes the temperature coefficient of the overall process rate and is a function of the activation energies of both chemical reaction and diffusion according to Eq. (5)

$$E = -R \left(\frac{d \ln k_{\text{ef}}}{dT^{-1}} \right) = \frac{E_{\text{D}} k_{\text{R}} + E_{\text{R}} k_{\text{D}}}{k_{\text{R}} + k_{\text{D}}} \quad (5)$$

where E_{R} and E_{D} are the activation energies of reaction and diffusion respectively. Equation (5) suggests that the experimental value of E may take on any values between E_{R} and E_{D} and that the exact value of E will depend on the region of experimental temperatures. Only if one of the two steps is much faster than another, the overall rate will be determined by slowest step and the experimental value of E will become the activation energy of this step, i.e., $E = E_{\text{R}}$ if $k_{\text{R}} \ll k_{\text{D}}$ (so-called kinetic regime) or $E = E_{\text{D}}$ if $k_{\text{D}} \ll k_{\text{R}}$ (so-called diffusion regime).

Traditionally, any value of E resulting from fitting experimental rate data to a rate equation (e.g., Eq. 2) is called misleadingly ‘the activation energy’. However, Eq. (5) clearly suggests that in the most general case the experimental value of E is not an activation energy of any of the two steps composing the overall process. In order to emphasize the difference between the experimental value of E and the theoretical activation energy the former is frequently referred to as an ‘effective’, or ‘apparent’, or ‘global’ activation energy.

The considered example is a simplified case of a condensed phase process that involves one chemical and one transport step. In reality such a process may involve multiple chemical steps as well as multiple transport steps. In this situation it may practically be impossible to obtain an equation that links the experimental value of E with the activation energies of the individual steps. However the nature of the relation between the values should be similar to that established by Eq. (5). That is in the general case the experimental value of E is a function of the activation energies of the individual steps and its particular value is determined by the contributions of the individual steps to the overall reaction rate. Therefore interpretation of E as the activation energy of an individual step should only be possible in the specific cases such as in case of the aforementioned kinetic or diffusion regime.

The next question is can we interpret the experimental value of A as the frequency factor? In the transition state theory the frequency factor is independent of the activation energy. As mentioned earlier, the experimental value of A is a scaling factor for the overall reaction rate. Increasing A corresponds to increasing the overall reaction rate. The same effect is accomplished by decreasing E . This fact suggests that experimental values of A and E may be correlated. Because fitting experimental data to a rate equation is usually accomplished by simultaneously adjusting the values of A and E , the values should be correlated in a compensating manner so that their simultaneous change does not affect the rate. This correlation is known as a compensation effect and is typically found in the following form

$$\ln A = aE + b \quad (6)$$

where a and b are constants.

Figure 3 depicts the experimental values of $\log A$ and E for the thermal decomposition of HMX that have been collected and reported by Brill *et al.* [11]. The data show a very strong correlation of the experimental values E and A . This situation is very typical and has been frequently reported in the literature. If for a particular process numerous values of E and A are not available in the literature, a good indication of the compensation effect at work may be the fact that

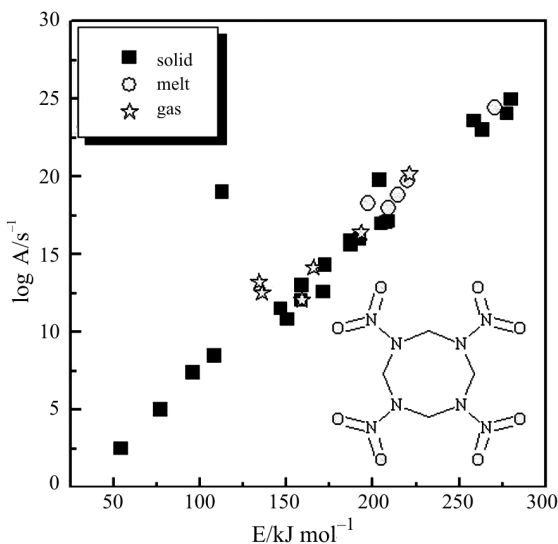


Fig. 3 Compensation effect for the thermal decomposition of HMX (chemical structure in inset) in different phases

reporting a larger value of E ($\sim 200 \text{ kJ mol}^{-1}$) is usually accompanied by a larger value of A ($\sim 10^{20} \text{ s}^{-1}$), and, vice versa, a smaller value of E ($\sim 50 \text{ kJ mol}^{-1}$) is normally reported with a smaller value of A ($\sim 10^5 \text{ s}^{-1}$). Anyway, unlike the theoretical values, the experimental values of E and A tend to be correlated that makes independent interpretation of both values impossible. Therefore, we face the question what value should we put our trust in? Obviously, in the value that is most likely to be correct, i.e., that is most stable under the compensation effect. It is clear from Fig. 3 that the experimental value of E is by far more stable than the experimental value of A . For instance, a tolerable change in E by 25% from 200 to 250 kJ mol^{-1} is accompanied by the enormous change in A of 5 orders of magnitude from 10^{17} to 10^{22} s^{-1} . Due to its large instability, the experimental value of A does not practically lend itself for any meaningful interpretations. For this reason, it makes more sense to concentrate the interpretative efforts on the experimental value of E and treat the experimental value of A as a dependent and inferior parameter.

Summarizing the discussion of interpretability of the experimental kinetic triplet we conclude that it does not seem reasonable to interpret the best-fit $f(\alpha)$ or $g(\alpha)$ model in terms of the reaction mechanisms and the experimental value of A in terms of the activated complex frequency. The most informative part of the triplet appears to be the experimental value of E . While not impossible, its interpretation in terms of activation energies may be quite challenging. The actual need for evaluating the whole kinetic triplet arises from the purely practical purpose of reproducing the experimental kinetic curves as well as of pre-

dicting kinetic curves outside the experimental temperature range.

Model-free kinetics

The cornerstone of the model-free approach to kinetic analysis is the use of the isoconversional principle. It states that at a constant extent of conversion the reaction rate is only a function of the temperature

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right] \equiv \left[\frac{d \ln k(T)}{dT^{-1}} \right] + \left[\frac{df(\alpha)}{dT^{-1}} \right] = -\frac{E_\alpha}{R} \quad (7)$$

The isoconversional methods make use of multiple heating programs (i.e., different heating rates or/and temperatures) because this is practically the only way to obtain data on the variation of the rate at a constant extent of conversion. Because the derivative of $f(\alpha)$ in Eq. (7) is zero, the isoconversional methods allow the E_α value to be determined without choosing the reaction model that eliminates the respective uncertainty (see above). Note that Eq. (7) is arrived at from the single step kinetic Eq. (2). However, unlike many other methods that assume a single Eq. (2) to hold throughout the whole region of experimental temperatures and extents of conversion, the basic assumption of the isoconversional methods is that a single Eq. (2) is applicable only to a single extent of conversion and the temperature region related to this conversion. In other words, the isoconversional methods describe the process kinetics by using multiple single step kinetic equations each of which is associated with a certain extent of conversion. For instance, the most popular isoconversional methods are the methods of Flynn and Wall [12] and Ozawa [13] that give rise to Eq. (8)

$$\ln(\beta) = \text{const} - \frac{1.05E_\alpha}{RT_\alpha} \quad (8)$$

where β is the heating rate and the E_α value is determined from the slope of the straight line $\ln(\beta)$ vs. T_α^{-1} . If a process under study obeys single step kinetics (Eq. (2)), Eq. (8) yields a series of parallel lines that have the same slope. As a result the E_α values do not vary with α . If the process involves multiple steps of different activation energies, the dependencies of $\ln(\beta)$ vs. T_α^{-1} can still be approximated by straight lines whose slope, however, changes systematically with α so that E_α demonstrates a systematic variation with α .

The Flynn and Wall and Ozawa methods introduce some systematic error in E_α when the value varies with α [14]. This error is eliminated in our advanced isoconversional method [14]. According to this method, for a set of n experiments carried out at

different arbitrary heating programs, $T_i(t)$ the E_α value is determined as the value that minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (9)$$

where

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (10)$$

The systematic error is eliminated by carrying out the integral in Eq. (10) over small time intervals. In Eq. (10) α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha$ which is usually taken to be 0.02.

There are two major misconceptions associated with the isoconversional methods. The first misconception arises from the fact that these methods frequently yield E_α that varies with α . Sometimes this fact is mistakenly perceived as a flaw of the methods because the result does not seem to meet the expectation of a constant value of the activation energy that is inspired primarily by undergraduate physical chemistry texts. The second misconception is associated with the fact that instead of the whole kinetic triplet the isoconversional methods produce only the values of E_α . This fact inspires the false belief that the isoconversional methods are not capable of producing an adequate kinetic description.

Speaking of the first misconception, we should make two important points. Firstly, the idea of a constant activation energy makes sense only for single-step gas phase reactions that occur in the absence of the reaction medium. In the presence of the medium (liquid or solid) the free energy barrier height becomes a function of physical parameters of the medium that in their turn change with the temperature [15]. Secondly, as mentioned above, the experimental value of E generally is not an activation energy of any single steps. It is rather a function of the activation energies of the individual steps and its particular value is determined by the contributions of the individual steps to the overall reaction rate. The contribution of the individual steps can change with the extent of conversion as well as with the temperature. Therefore, there is nothing wrong with the experimental value of E_α varying with α . It is simply an indication that the process under study is multi-step kinetics.

With regard to the second misconception we should recall that the complete kinetic triplet is usually obtained for the theoretical purposes of interpretation and for the practical purposes of describing the original kinetics and predicting kinetics outside the experimental temperature region. As mentioned earlier, the theoretical value of the experimental kinetic triplet is not very high and of the whole triplet the ex-

perimental values of A and $g(\alpha)$ or $f(\alpha)$ are the least likely to be physically interpretable. Therefore, from the theoretical standpoint not producing the values of A and $g(\alpha)$ or $f(\alpha)$ is not much of a loss, if any. On the other hand, analysis of the E_α -dependence may suggest some very helpful clues about the activation energies of the individual steps as well as about the reaction mechanism [8, 15, 16]. Furthermore, model-free kinetics does not need the experimental values of A and $g(\alpha)$ or $f(\alpha)$ for the practical purposes of kinetic predictions. The respective predictive equation [17, 18] was originally given in the following form

$$t_\alpha = \frac{\frac{1}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dT}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (11)$$

and later modified to employ arbitrary heating program data for predicting isothermal kinetics as follows

$$t_\alpha = \frac{J[E_\alpha, T(t_\alpha)]}{\exp\left(\frac{-E_\alpha}{RT_0}\right)} \quad (12)$$

Predictions made by Eqs (11) and/or (12) can be called ‘model-free predictions’ because they do not require knowledge of the reaction model (or the preexponential factor). It has been experimentally demonstrated [4, 18] that the model-free equations give rise to reliable predictions, as kinetic predictions based on fitting single heating rate data (e.g., Eq. (3)) fail.

Therefore, in model-free kinetics the sole use of the E_α -dependence allows one to accomplish the aforementioned theoretical and practical goals. As a result, model-free kinetics turn the experimental values of A and $g(\alpha)$ or $f(\alpha)$ into unnecessary kinetic entities. However, if ‘multiplying entities without necessity’ makes one feel more at ease with model-free kinetics, the experimental values A and $g(\alpha)$ or $f(\alpha)$ can be determined by using some rather simple methods [18]. For instance, the values of A_α can be estimated by substituting the values of E_α in Eq. (6). An example of the application of this method can be found in our recent paper [9]. Once the values of A_α are known, one can evaluate the reaction model in its integral form as

$$g(\alpha) = A_\alpha J[E_\alpha, T(t_\alpha)] \quad (13)$$

or in its differential form as

$$f(\alpha) = \frac{d\alpha/dt}{A_\alpha \exp\left(\frac{-E_\alpha}{RT}\right)} \quad (14)$$

Therefore model-free kinetics is perfectly capable of determining the complete kinetic triplet.

Conclusions

Model-free kinetics rests on evaluating the E_α -dependence. This dependence is adequate for theoretical purposes of kinetic interpretation as well as for the practical purposes of kinetic predictions. Normally, model-free kinetics do not concern with evaluating A and $g(\alpha)$ or $f(\alpha)$ because they are not needed for performing kinetic predictions. Also, these values are hardly suitable for theoretical interpretation because of the strong ambiguity associated with them. However these values can be determined in the frameworks of model-free kinetics.

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