
Review

A review of the mutual dependence of Arrhenius parameters evaluated by the thermoanalytical study of solid-state reactions: the kinetic compensation effect

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Received 7 December 1993; accepted 20 March 1994

Abstract

The kinetic compensation effect (KCE) has been observed in numerous kinetic studies of solid-state reactions using thermoanalytical methods. An attempt has been made to separate phenomenologically the KCE into the variation and the mutual dependence of the resultant Arrhenius parameters. The probability of the mutual dependence of the Arrhenius parameters caused by the properties of the general kinetic equation was discussed in relation to: (1) the reaction temperature interval, (2) the fractional reaction α , (3) the kinetic model function $f(\alpha)$, and (4) the isokinetic hypothesis. The mutual dependence of the Arrhenius parameters due to the properties of the general kinetic equation was first checked before discussing the KCE in relation to a physico-chemical factor for a series of reactions under investigation. The necessity of establishing a check system for the kinetic calculation is discussed briefly on the basis of the prerequisites of the methods of kinetic calculation and the properties of the general kinetic equation.

Keywords: Arrhenius; CRTA; Isokinetic; KCE; Kinetics; Solid state; TA

1. Introduction

On determining the kinetic parameters from the thermoanalytical (TA) curves of solid-state reactions, we sometimes encounter variations in the kinetic parameters

due to the sample and measuring conditions. It is easily understood that variation in the Arrhenius parameters results from a certain change in the overall behavior of the reaction process due to these factors. Further analysis of the variation of kinetic parameters for a series of reactions leads to a general result of a mutual dependence of the apparent Arrhenius parameters known as the kinetic compensation effect (KCE) [1] expressed by

$$\ln A_{\text{app}} = aE_{\text{app}} + b \quad (1)$$

Eq. (1) indicates the linear dependence between the apparent values of the logarithmic pre-exponential factor $\ln A_{\text{app}}$ and the apparent activation energy E_{app} with the constants a and b . The simple relationship of Eq. (1) is reproduced on the Arrhenius coordinate, $\ln k$ vs. $1/T$, with an intersection point called the isokinetic point ($1/T_{\text{iso}}$, $\ln k_{\text{iso}}$) [2]. Using the isokinetic relationship, Eq. (1) is rewritten as

$$\ln A_{\text{app}} = \frac{E_{\text{app}}}{RT_{\text{iso}}} + \ln k_{\text{iso}} \quad (2)$$

Fig. 1 shows such a relationship of the mutual dependence of the kinetic parameters.

1.1. Historical

Numerous papers have dealt with the variations of the apparent Arrhenius parameters using Eqs. (1) and (2). Although the present state of understanding of the KCE can be found in many historical surveys [3–6], causation of the KCE may be classified into the following three categories.

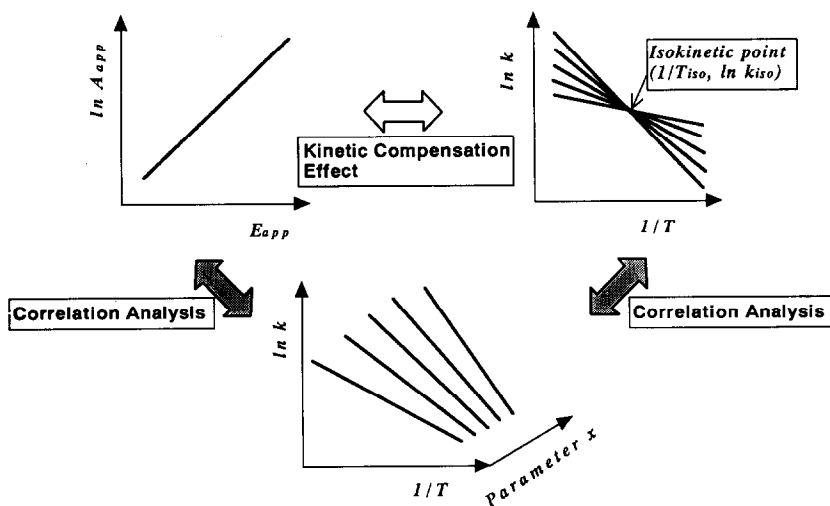


Fig. 1. A schematic representation of the mutual dependence of the Arrhenius parameters.

Physico-chemical properties of the samples and reaction processes

A typical example of the physico-chemical interpretation of the KCE is seen for the thermal decomposition of CaCO_3 under various partial pressures of CO_2 . In 1935, Zawadski and Bretzsnajder [7] originally pointed out the partial pressure dependent variation in E_{app} . A theoretical interpretation for the partial pressure dependence was attempted by Pavlyuchenko and Prodan [8], showing a functional dependence of E_{app} on the partial pressure of CO_2 . The kinetic behavior was reinvestigated experimentally by Wist [9] and analyzed by Roginski and Chajt [10] from a viewpoint of chemical statistics. Such a physico-chemical interpretation of the KCE belongs to a procedure of “correlation analysis [11]”, i.e. a mathematical treatment starting from experimental data and seeking empirical relationships which can subsequently be interpreted theoretically, see Fig. 1. Specifying the physico-chemical variables, other than reaction rate and temperature, such as partial pressure of a gas [12], bond energy due to the different metals and ligands [13–15], defect concentration [16,17], chemical composition [18], impurity [19], etc., has been attempted to explain the empirical KCE. In the practice of TA kinetics, however, the physico-chemical properties of the process influencing the kinetic parameters are hard to identify quantitatively, because of the macroscopic character of the kinetic data derived from TA curves. Without quantitative identification of the physico-chemical property, estimation of the linear interdependence of Eq. (1) does not provide meaningful kinetic interpretation, but only shows an empirical observation of the mutual dependence of the Arrhenius parameters.

Experimental procedural factors in the TA measurements

It is generally accepted that the experimentally resolved shape of a TA curve changes with the measuring conditions applied, such as sample mass, heating rate, atmosphere, etc. [20]. In many cases, the kinetic parameters obtained from such a TA curve are also dependent on the measuring conditions applied, showing empirically the KCE. Guarini et al. pointed out [21] that non-linearity of the Arrhenius plot increases with the sample mass, and recommended extrapolation to zero mass to avoid the KCE. Sample mass dependent variation in the apparent Arrhenius parameters has been explained by the effect of gradients in temperature and gaseous pressure [22]. The KCE caused by the effect of heating rate is rather common for the thermal decomposition of solids with gaseous products [23–25]. On discussing the KCE obtained from different measuring conditions, both the physico-chemical effects of the applied conditions and the changes in the self-generated reaction conditions by the reaction itself should be taken into account. The latter is closely connected with the reliability of the experimentally resolved shape of the TA curve as a source of kinetic data [26,27], because such a self-generated reaction condition is not controlled, in a strict sense, in conventional TA measurements. A typical example can be seen for the effect of atmospheric conditions, in which a change in the atmospheric conditions is accompanied by the consequent change in the self-generated atmospheric conditions.

Mathematical consequences of the general kinetic calculation

Discussion of the mutual dependence of the Arrhenius parameters has also been attempted from the mathematical and statistical points of view. Because the Arrhenius parameters have meaning only in relation to the kinetic model function, these are distorted by an inappropriate kinetic model function. Criado and Gonzalez reported [28] that sets of Arrhenius parameters calculated using inappropriate kinetic model functions show mutual dependence. The degree of the distortion was further discussed on the basis of an empirical analysis [29–31] and a mathematical approximation [32]. Reexamination of the KCE of this type was performed by Somasekharan and Kalpagam [33], who suggested the correspondence between the isokinetic temperature and the maximum TA peak.

However, application of the Arrhenius equation to complicated solid-state processes has been questioned [34]. Hullet made a search for the non-linearity of the Arrhenius plot [35], determining that any deviations from a straight line in the plot of $\ln k(T)$ vs. $1/T$ are to be considered as almost certain evidence that the observed process is complex. Drawing the theoretical TA curves, correlation of the Arrhenius parameters and its effect on the TA curves were noticed by Šesták [36] and further analyzed by Zsakç [37]. Exner first suggested [38] that it is not correct to determine the KCE by a linear regression of E_{app} vs. $\ln A_{\text{app}}$, because these quantities are mutually dependent. Šesták suggested [39] that the extent of the interdependence of the Arrhenius parameters may be characterized, among others, by the angle of the functions E/RT and $\ln A$ in Hilbert space. This angle also depends on the temperature interval. Agrawal proposed dividing the KCE into two groups by the existence of an isokinetic point: one arising from physico-chemical factors and the other from computational and experimental artifacts [40]. Because $k(T)$ and T can be determined independently, the plot of $\ln k(T)$ vs. $1/T$ is statistically correct. However, Agrawal's procedure of distinguishing a false KCE from a true one was criticized by Šesták [41] and was shown by Zsakç and Somasekharan to be incorrect [42]. Although it is reasonable to exclude the KCE that does not exhibit an isokinetic point from the present argument, there is no physical explanation for such a KCE resulting from physico-chemical factors. Garn's standpoint is that the KCE is simply a consequence of trying to describe a complex process by computing the Arrhenius parameters, accepting changes of many orders of magnitude without question or test [43].

1.2. Interaction of the causations

Fig. 2 shows schematically a procedure of TA kinetics resulting in the KCE. According to the procedure of TA kinetics of solid-state reactions, the physico-chemical causations and the resulting mutual dependence of the Arrhenius parameters seem to be interpreted separately [44]. The TA curve is a response of a certain averaged behavior of the respective reaction steps involved, as is shown schematically in Fig. 3 for the case of the thermal decomposition of solids. The mutual relationship of the consecutive and/or concurrent steps may change with the experimental conditions applied and the self-generated reaction conditions, influ-

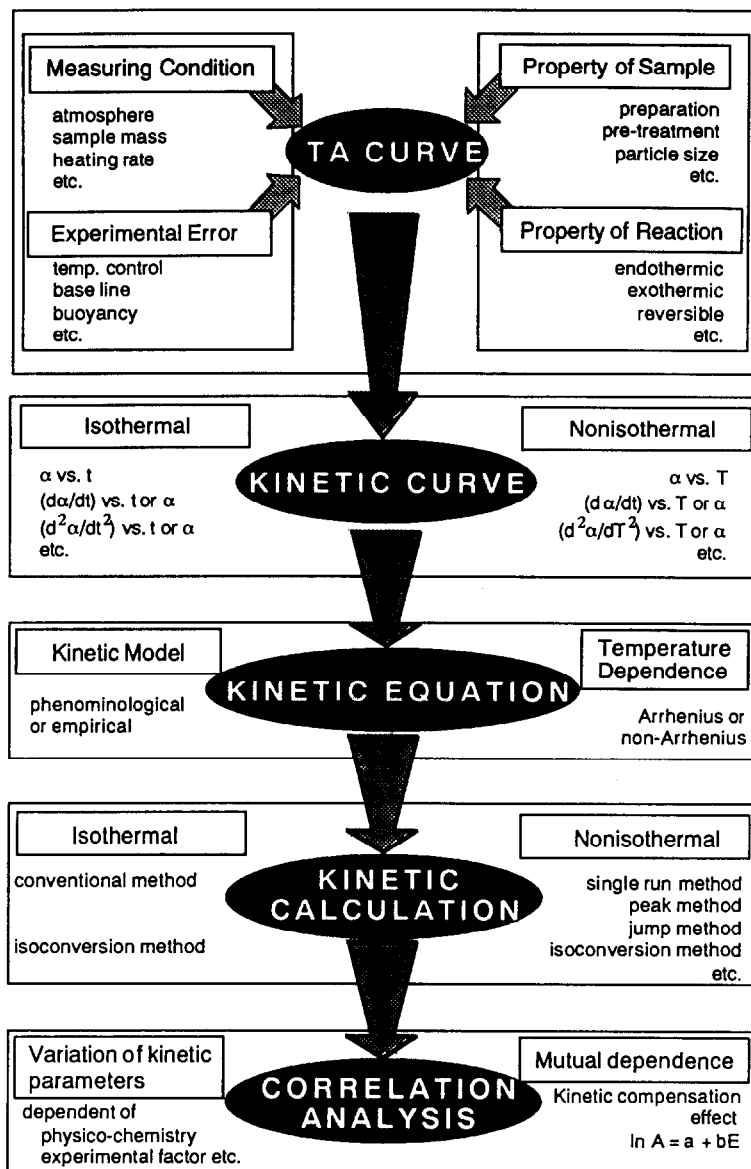


Fig. 2. A schematic diagram of the procedure of TA kinetics.

encing the overall characteristics of the reaction. The variation in the overall behavior for a reaction is only detected as changes in the position and shape of the experimentally resolved TA curves. The kinetic parameters calculated from these macroscopic data are projected on the Arrhenius coordinates through a particular projection system, i.e. the general kinetic equation. The variation in the respective

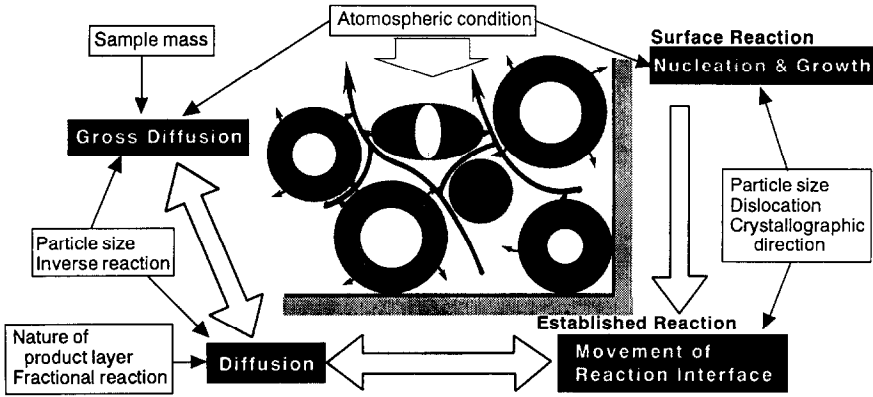


Fig. 3. A diagram of the physico-chemical processes of the thermal decomposition of solids in a matrix.

kinetic parameters apparently results from changes in the experimental and physico-chemical factors. However, the resulting mutual dependence of the Arrhenius parameters, usually stated as the KCE, seems to be connected with the properties of the general kinetic equation. In such a case, not knowing the properties of the general kinetic equation concerning the KCE, interpretation of the mutually dependent variation of the Arrhenius parameters connected with the physico-chemical properties of the kinetic process is likely to lead to a speculative conclusion.

It is thus necessary to clarify the relationships existing between the TA curves and the general kinetic equation, before discussing these mutual dependence relationships connected directly to the physico-chemical properties of the kinetic process under investigation. In this paper, the probability of the mutual dependence of the Arrhenius parameters caused by the properties of the general kinetic equation is discussed in relation to: (1) the reaction temperature interval, (2) the fractional reaction α , (3) the kinetic modal function $f(\alpha)$, and (4) the isokinetic hypothesis. The necessity of establishing a check system for the standard kinetic calculation is proposed on the basis of the prerequisites of the methods of kinetic calculation and the properties of the general kinetic equation. It is hoped that the present discussion on the KCE will lead to improved analyses of TA kinetic data.

2. General kinetic equation

Here we consider the following general kinetic equation

$$\frac{d\alpha}{dt} = A_{\text{app}} \exp\left(-\frac{E_{\text{app}}}{RT}\right) f(\alpha) \quad (3)$$

with

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad k(T) = A_{\text{app}} \exp\left(-\frac{E_{\text{app}}}{RT}\right)$$

where α , t , R and T are the fractional reaction, time, gas constant and temperature, respectively; and $f(\alpha)$ is the kinetic model function derived originally on the basis of a physico-geometric assumption concerning the movement of the reaction interface under isothermal conditions. Eq. (3), composed of an $f(\alpha)$ -dependent rate constant, and the Arrhenius equation, are widely used when determining the kinetic parameters from TA curves, not only for traditional isothermal reactions but also for reactions under linearly changing temperatures or with a controlled transformation rate. Simple application of Eq. (3), proposed originally under isothermal conditions, to any non-isothermal conditions is generally inaccurate. Appropriate integration under non-isothermal conditions [45] requires temperature-dependent integration limits of the Arrhenius rate constant [46,47] leading to introduction of the so-called $p(x)$ function [48], i.e. $p(x) = \exp(x)\pi(x)/x$. Only when the approximation of the $p(x)$ is roughly constant are the resultant equations analogous to those derived isothermally [49], differing only by a multiplication constant. In the following subsections, probable reasons for the mutual dependence of the resultant Arrhenius parameters are discussed by assuming practical applications of Eq. (3) to the TA curves of isothermal and non-isothermal reactions.

2.1. Reaction temperature interval

The reaction temperature interval is a procedural term in isothermal TA measurements, although it is regulated by the properties of the reaction under investigation. This is also accepted as the experimental variable especially for the non-isothermal run, because the temperature interval is influenced by the sample and experimental conditions applied. Unfortunately, the temperature interval is not considered in the kinetic analysis of TA curves.

It is sometimes observed in the case of a KCE established among the Arrhenius parameters obtained from more than one TA curve under various sample and measuring conditions, that the changes in E_{app} and $\ln A_{\text{app}}$ are always accompanied by a change in the working temperature interval of the kinetic analysis ΔT [49]. Fig. 4(a) represents a practical example of the $1/\Delta T$ dependence of the apparent Arrhenius parameters obtained at different heating rates for the non-isothermal dehydration of crushed crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [50]. The consequence mutual dependence of the Arrhenius parameters is shown in Fig. 4(b). The apparent values of E_{app} and A_{app} are written as follows, using the lowest temperature T_{L} , the highest temperature T_{H} and the temperature interval $\Delta T = T_{\text{H}} - T_{\text{L}}$ [51]

$$E_{\text{app}} = \frac{RT_{\text{H}}T_{\text{L}}}{\Delta T} \ln X \quad (4)$$

$$\ln A_{\text{app}} = \frac{1}{T_{\text{iso}}} \frac{T_{\text{H}}T_{\text{L}}}{\Delta T} \ln X + \ln k_{\text{iso}} \quad (5)$$

where X depends on the calculation method. Table 1 lists the form of X for the respective methods of kinetic calculation. The variation in the value of $\ln X$ among a series of TA curves is relatively small compared with that in the value of

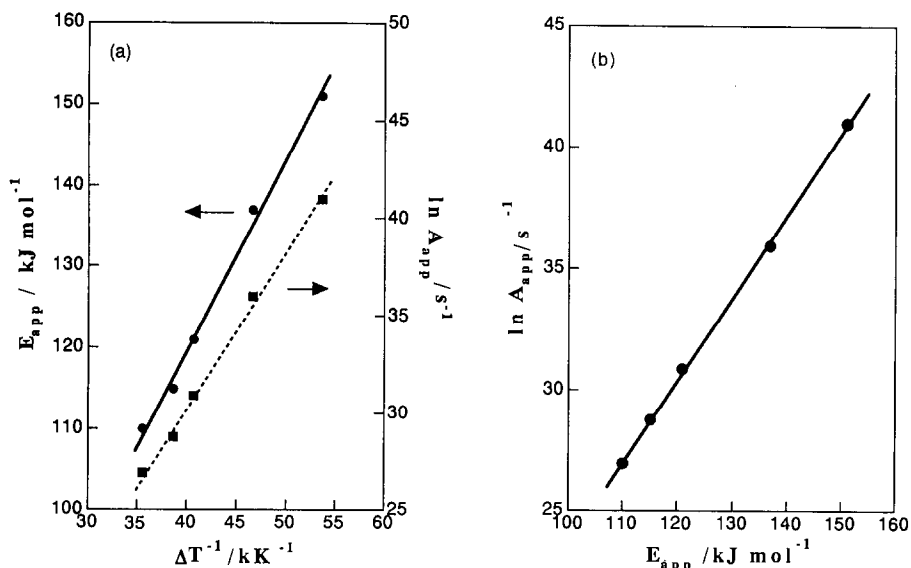


Fig. 4. Mutual dependence of the Arrhenius parameters, E_{app} and A_{app} , with the working temperature interval ΔT for the non-isothermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

Table 1

The form of X in Eqs. (4) and (5) for the respective method of kinetic calculation

Method	X in differential form	X in integral form
Isothermal methods	$\frac{(d\alpha/dt)_H}{(d\alpha/dt)_L}$	$\frac{t_H(\alpha)}{t_L(\alpha)}$
Non-isothermal single run methods	$\frac{(d\alpha/dT)_H f(\alpha_L)}{(d\alpha/dT)_L f(\alpha_H)}$	$\frac{g(\alpha_L) T_H^2}{g(\alpha_H) T_L^2}$ ^{a, b}
Non-isothermal isoconversion methods	$\frac{(d\alpha/dT)_H \phi_H}{(d/dT)_L \phi_L}$	$\frac{\phi_H T_L^2}{\phi_L T_H^2}$ ^c
Non-isothermal peak method	$\frac{f'(\alpha_L) T_L^2 \phi_H}{f'(\alpha_H) T_H^2 \phi_L}$	–
CRTA Jump method	$\frac{(d\alpha/dt)_H}{(d\alpha/dt)_L}$	–

^a The Coats–Redfern equation [52]. ^b $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$. ^c The Kissinger–Akahira–Sunose-type equation [53].

$T_H T_L / \Delta T$, owing to a mathematical consequence of the exponential form of the Arrhenius equation. This implies that a constant value of $T_H T_L / \Delta T$ is a necessary condition for obtaining a constant value of E_{app} [54]. In this case, however, a constant value of $\ln A_{\text{app}}$ is not necessarily obtained [55]; the constant value of ΔT can yield constant Arrhenius parameters. These relationships are easily confirmed

by the theoretical plots of TA curves [56]. Thus, for a smaller ΔT , even the change in $T_H T_L$ can be ignored in comparison with the change in $1/\Delta T$. In contrast to the requirement of a wide temperature interval for reliable determination of the Arrhenius parameters, a narrow range of temperature is sometimes necessary to satisfy a practical requirement. In such a case, the values of E_{app} and $\ln A_{app}$ should be functions of $1/\Delta T$. In this sense, a KCE of this type can be understood as a projection of the interrelationship among $\ln A$, E and ΔT onto the $\ln A$ vs. E plane [57]. A change in one of three parameters is thus compensated by the change in the other parameters, reproducing the empirical linear relationship between the values of E_{app} and $\ln A_{app}$. Although kinetic use of controlled transformation rate thermal analysis (CRTA) [58] has an advantage due to better control of the self-generated reaction conditions [59], the ΔT dependence is also expected for the E_{app} value determined from the CRTA curve using the Jump method [60], because Eq. (4) itself is used for the calculation (see Table 1). It has also been pointed out by Fatu and Segal [61] that interdependence of the kinetic parameters obtained from the CRTA curves is expected from the general kinetic equation.

Usually non-isothermal kinetic plots for determining the apparent values of E_{app} and A_{app} from a single TA curve consist of the vertical axis including the rate of transformation and the horizontal axis of reciprocal temperature $1/T$. When the kinetic parameters are determined for the reaction under linearly increasing temperature, the rate of transformation is normalized among those of different heating rate ϕ , i.e. $(d\alpha/dt)/\phi = d\alpha/dT$. However, the variation in the horizontal axis caused by different ϕ values, characterized among others by $1/\Delta T$, is not normalized because of the exponential form of the Arrhenius equation. When the ΔT is small enough, the variation in the apparent Arrhenius parameters is a mathematical consequence of the variation of $1/\Delta T$.

2.2. Fractional reaction α

The extent of reaction is the fundamental concept in formulating the kinetic equation. The fractional reaction α , usually the molar fraction of the product to that of the original reactant, is generally employed in heterogeneous reactions instead of the concentration terms used in homogeneous reactions. It is believed implicitly that the value of α is a generalized measure of the extent of reaction and that the procedure does not influence the kinetic parameters calculated. Within the regime of the KCE, however, some problems can be identified in connection with the sample mass dependent and/or particle size dependent variation of the kinetic parameters [62,63].

If the volume of the original phase of a sample particle with spherical symmetry is contracted by moving the reaction interface from the original surface, the value of α is defined as

$$\alpha = \frac{r_0^3 - r^3}{r_0^3} \quad (6)$$

where r_0 and r are radii of the reactant particle at time $t = 0$ and $t = t$, respectively. When the movement of the reaction interface is regulated by chemical reaction, the value of r is expressed by

$$r = r_0 - k_s t \quad (7)$$

where k_s is a specific rate constant. Combining Eqs. (6) and (7), we obtain

$$1 - (1 - \alpha)^{1/3} = \frac{k_s t}{r_0} \quad (8)$$

which is the R_3 law in an integral form. Assuming the Arrhenius type of temperature dependence of k_s , the temperature dependence of the apparent rate constant k_{app} for the R_3 law is expressed by

$$k_{app} = \frac{A}{r_0} \exp\left(-\frac{E}{RT}\right) = \left(\frac{4\pi\rho}{3m_0}\right)^{1/3} A \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where m_0 is the initial mass of one particle and ρ is the volume density. Accordingly, the apparent pre-exponential factor A_{app} is dependent on the mass and/or radius of the sample particle. A similar dependence is observed for the other reactions of contracting geometry type, e.g. the contracting cube equation. For these, the apparent values of k_{app} and A_{app} with respect to the specific values k_s and A_s are listed in Table 2. Fig. 5 shows the variation of k_{app} with the values of r_0 and m_0 as the ratio to the specific values. The multiplication constants of the r_0 - and m_0 -dependent k_{app} and A_{app} are set to unity by the specific values of r_s and m_s . On determining the apparent kinetic parameters from a set of parallel isothermal TA

Table 2

The multiplication constant of r_0 and/or m_0 -dependent k_{app} and A_{app} with respect to the specific k_s and A_s

Rate-controlling step	Shrinkage dimension	r_0 dependence	m_0 dependence	Symbol
Chemical event	1	$\frac{1}{r_0}$	$\frac{S\rho^{a,b}}{m_0}$	R_1
	2	$\frac{1}{r_0}$	$\left(\frac{2\pi L\rho}{m_0}\right)^{1/2c}$	R_2
	3	$\frac{1}{r_0}$	$\left(\frac{4\pi\rho}{3m_0}\right)^{1/3}$	R_3
Diffusion	1	$\frac{1}{r_0^2}$	$\left(\frac{S\rho}{m_0}\right)^{2a,b}$	D_1
	2	$\frac{1}{r_0^2}$	$\frac{2\pi L\rho^c}{m_0}$	D_2
	3	$\frac{1}{r_0^2}$	$\left(\frac{4\pi\rho}{3m_0}\right)^{2/3}$	D_3

^a r_0 is not the radius but the thickness of the plate-like sample. ^b S is the area of reaction interface. ^c L is the length of the rod-like sample.

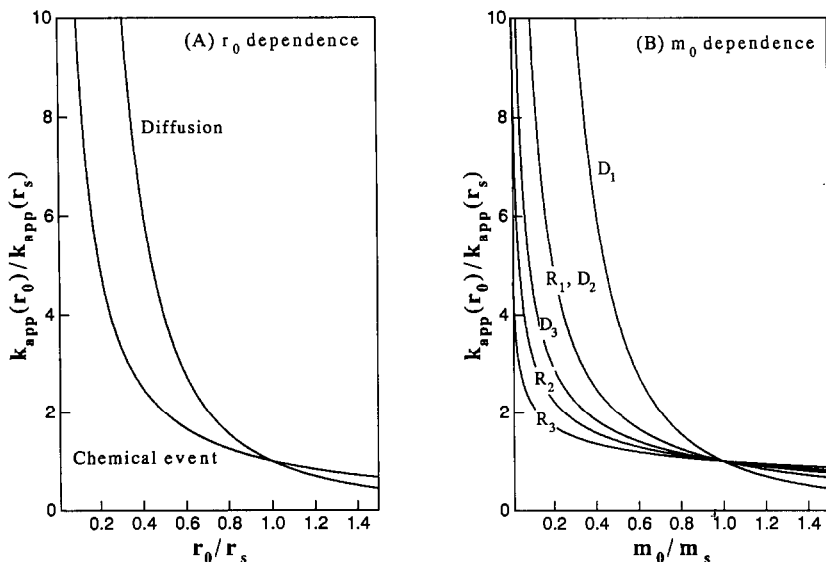


Fig. 5. The variation of the apparent rate constant k_{app} with the values of r_0 and m_0 .

curves, the value of E is expected theoretically to be independent of m_0 and r_0 because of the same m_0 and/or r_0 dependence of k_{app} and A_{app} with respect to the respective specific values. In practice, however, a slight but detectable decrease in both the apparent values of E_{app} and A_{app} is sometimes observed with increasing m_0 and r_0 [64]. Flanagan et al. [65] and Guarini et al. [21] have proposed that the reciprocal apparent rate constant and the fractional reaction, respectively, extrapolated to zero mass using empirical linear relationships in connection with sample mass. By using in the Arrhenius plot a specific rate constant reduced by the relation in Table 2, the unexpected variation of E_{app} is avoided, yielding simultaneously a unique value of the pre-exponential factor, independent of m_0 and r_0 .

Similarly, the A_{app} value for the reaction of contracting geometry type under a linearly increasing temperature is also dependent on m_0 and r_0 [66]. This dependence can generally be expressed by

$$A_{app} = \frac{A_s}{r_0^{1/e}} = C \frac{A_s}{m_0^{1/de}} \tag{10}$$

where e is a kinetic exponent of interface advancement ($e = 1$ for the linear law and $e = 1/2$ for the parabolic law), d is the dimension of interface contraction and C is a constant. The following kinetic expression is obtained from Eqs. (3) and (10)

$$\frac{d\alpha}{dt} m_0^{1/de} = CA_s \exp\left(\frac{E}{RT}\right) f(\alpha) \tag{11}$$

Assuming that the kinetic obedience is constant irrespective of m_0 and r_0 , Eq. (11) is considered as the normalized kinetic equation, from which specific Arrhenius

parameters are derived. For the Arrhenius parameters calculated using Eq. (11) from the non-isothermal TA curves of different m_0 and r_0 , however, the variation in E_{app} values seems still to be observed due to the change in the reaction temperature interval induced by the different m_0 and r_0 [67], as in the case of the effect of heating rate described above.

2.3. Kinetic model function $f(\alpha)$

Because the rate constant is characteristic for the $f(\alpha)$ assumed, the Arrhenius parameters are mutually correlated with the $f(\alpha)$. Mis-estimation of the kinetic model function thus results in the distortion of the apparent Arrhenius parameters from the specific values. For example the popular Freeman and Carroll method [68], derived by assuming the reaction order model $(1 - \alpha)^n$, always gives the apparent exponent n_{app} regardless of the true kinetic model and consequently distorts the apparent Arrhenius parameters. Such a distortion in the apparent value of E_{app} and A_{app} from the true value of E and A , due to the use of an inappropriate kinetic model function $F(\alpha)$ instead of the appropriate function $f(\alpha)$, is expressed by [69]

$$\frac{E_{\text{app}}}{E} = \frac{f(\alpha_p)F'(\alpha_p)}{F(\alpha_p)f'(\alpha_p)} \quad (12)$$

with

$$f'(\alpha) = \frac{df(\alpha)}{d\alpha} \quad F'(\alpha) = \frac{dF(\alpha)}{d\alpha}$$

and

$$\ln \frac{A_{\text{app}}}{A} = \frac{E}{RT_p} \left[\frac{f(\alpha_p)F'(\alpha_p) - F(\alpha_p)f'(\alpha_p)}{F(\alpha_p)f'(\alpha_p)} \right] + \ln \frac{f(\alpha_p)}{F(\alpha_p)} \quad (13)$$

where subscript p indicates the values corresponding to the maximum of the TA peak. The distortion of the Arrhenius parameters by the use of an n th order model instead of the true kinetic model is represented in Table 3. Detailed analysis indicates that the values of n_{app} is characteristic for the $f(\alpha)$, but α_p also depends on the $x_p = E/RT$. Therefore the value of E_{app}/E increases slightly with increasing x_p for the $f(\alpha)$ of diffusion-controlled models [70]. However, the E_{app}/E ratio decreases with increasing x_p for the A_m model according to the equation [71]

$$\frac{E_{\text{app}}}{E} = \frac{m - 1}{x_p \pi(x_p)} + 1 \quad (14)$$

where m is the true kinetic exponent of the A_m model and $\pi(x)$ is the approximation of the temperature integral [48].

Although it does not seem to have any physico-chemical importance, the KCE arising from a single non-isothermal TA curve by the use of various inappropriate kinetic model functions has been reported by many workers [28–33]. Somasekharam and Kalpagam reported [33] that in this type of KCE the T_{iso} in Eq. (2) closely corresponds to the peak temperature T_p of the TA curve. The above

Table 3

The ratio of distortion of the Arrhenius parameters distorted by the use of the n th order model $(1 - \alpha)^n$ instead of the true kinetic model of the diffusion-controlled $D_L(\alpha)$ and of the Avrami–Erofeyev $A_m(\alpha)$

$f(\alpha)$	E_{app}/E	$\ln(A_{app}/A)$
D_1	$\frac{n\alpha_p}{(1 - \alpha_p)}$	$\frac{E}{RT_p} \left(\frac{n\alpha_p}{1 - \alpha_p} - 1 \right) + \ln \frac{1}{2\alpha_p(1 - \alpha_p)^n}$
D_2	$-n \ln(1 - \alpha_p)$	$\frac{E}{RT_p} [-n \ln(1 - \alpha_p) - 1] + \ln \left[\frac{-1}{(1 - \alpha_p) \ln(1 - \alpha_p)} \right]$
D_3	$\frac{-3n[1 - (1 - \alpha_p)^{1/3}]}{(1 - \alpha_p)^{1/3} - 2}$	$\frac{E}{RT_p} \left\{ \frac{-3n[1 - (1 - \alpha_p)^{1/3}]}{(1 - \alpha_p)^{1/3} - 2} - 1 \right\} + \ln \frac{3(1 - \alpha_p)^{(2/3) - n}}{2[1 - (1 - \alpha_p)^{1/3}]}$
D_4	$3n[1 - (1 - \alpha_p)^{1/3}]$	$\frac{E}{RT_p} \{3n[1 - (1 - \alpha_p)^{1/3}] - 1\} + \ln \frac{3}{2(1 - \alpha_p)^n[(1 - \alpha_p)^{-1/3} - 1]}$
A_m	$\frac{-m\alpha_p[-\ln(1 - \alpha_p)]}{m - m[-\ln(1 - \alpha_p)] - 1}$	$\frac{E}{RT_p} \left\{ \frac{-m\alpha_p[-\ln(1 - \alpha_p)]}{m - m[-\ln(1 - \alpha_p)] - 1} - 1 \right\} + \ln \frac{m[-\ln(1 - \alpha_p)]^{1 - 1/m}}{(1 - \alpha_p)^{n - 1}}$

relationships for the distortion of Arrhenius parameters by an inappropriate kinetic model function indicate that such a plot of $\ln A_{app}$ vs. E_{app} has a slope of $1/RT_p$, only when the logarithmic term $\ln[f(\alpha_p)/F(\alpha_p)]$ in Eq. (13) is close to zero. Because the values of the logarithmic terms change with $F(\alpha_p)$, the slope differs from $1/RT_p$, depending on the $F(\alpha_p)$ used. In the case of establishing the KCE with the use of various $F(\alpha_p)$, the slope of the KCE is a certain mean value determined from the relationship between the $f(\alpha_p)$ and $F(\alpha_p)$ examined. This explains the empirical fact that a KCE of this type does not indicate a single intersecting point on the Arrhenius coordinate, i.e. an isokinetic point. Accordingly, it is sometimes called a “false” and/or “superficial” KCE [51,55].

One of the most important problems concerning the kinetic model function is whether or not the widely used kinetic model function can describe the real process of the reaction under investigation, because any difference between the theoretical model and the real process leads to the distortion of the Arrhenius parameters according to Eqs. (12) and (13). Introducing the accommodation function $a(\alpha)$ [72], the discrepancy of the idealized $f(\alpha)$ from the true function $h(\alpha)$ of a real process can be expressed as

$$h(\alpha) = f(\alpha)a(\alpha) \tag{15}$$

Then the kinetic expression $h(\alpha)$ can be regarded as the distorted case of homogeneous-like kinetics and of $f(\alpha)$, with a possible $a(\alpha)$ to decrease the difference in the idealized $f(\alpha)$ from the practical process. The simplest example of the accommodation is the application of non-integral exponents into the $f(\alpha)$, which has been used practically to determine the best fit of the functional dependence of a kinetic curve [73]. From a simple geometric consideration, the non-integral kinetic exponent is understood as relating to the “Fractal” dimension [74].

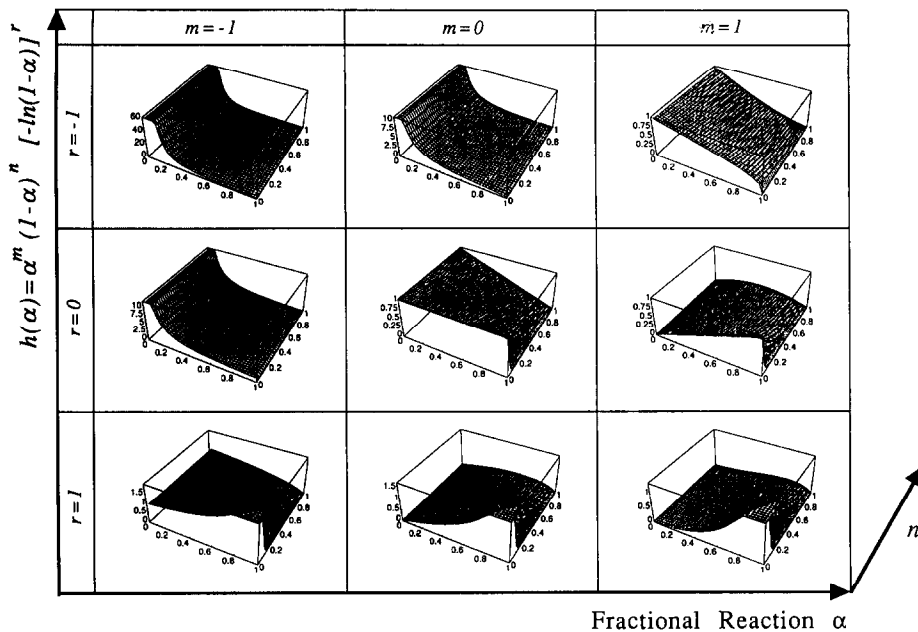


Fig. 6. The dependence of the Šesták–Berggren function $h(\alpha)$ on the kinetic exponents m , n and r .

It is apparent, however, that accommodation of the more complicated process in $h(\alpha)$ is extremely difficult based on the real physical chemistry and is possibly expressed by the empirical (analytical) formula. Such an empirical function containing three kinetic exponents, so that there is some flexibility in describing real TA data as closely as possible, is shown as the Šesták–Berggren (SB) model [75]

$$h(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^r \quad (16)$$

Eq. (16) can also be understood in terms of $a(\alpha)$, where $a(\alpha)$ bears the form of either of the functions α^m , $(1 - \alpha)^n$ and/or $[-\ln(1 - \alpha)]^r$. Fig. 6 represents the dependence of the $h(\alpha)$ function on the kinetic exponents m , n and r , assuming $(1 - \alpha)^n$ as the $f(\alpha)$, and α^m and/or $[-\ln(1 - \alpha)]^r$ as the $a(\alpha)$. The SB model serves particularly to fit the prolonged reaction tails due to the actual behavior of real particles and can match the particle non-sphericity in view of the morphological description in terms of the characteristic dimensions (usually the longest particle length), interface (the average boundary) and volume (the mean section area). Although in such a kinetic approach the physico-geometric features of the process as assumed in formulating the $f(\alpha)$ are difficult to predict because of the complicated functional dependence in Eq. (16), it is useful to avoid distortion of the Arrhenius parameters by the use of an inappropriate kinetic model function. Recently, a calculation method for the kinetic exponents of an empirical function was proposed by Malek [76], employing the two-parameter SB model

$$h(\alpha) = \alpha^m (1 - \alpha)^n \quad (17)$$

2.4. Isokinetic hypothesis

The applicability of conventional kinetic analysis of the TA curve relies upon the “isokinetic hypothesis”, i.e. the kinetic obedience remains constant during the course of the reaction under the temperature conditions applied. This prerequisite is not always satisfied with a practical set of TA curves. The application of conventional kinetic analysis beyond this prerequisite leads to distortion of the apparent Arrhenius parameters, which requires a correction [77].

Typical examples can be seen for the crystallization processes of amorphous solids and glasses [77,78]. The crystallization kinetics is interpreted as consisting of the consecutive and/or concurrent processes of nucleation and growth [1,79], in which the total activation energy is the sum of the partial energies of nucleation, growth and diffusion [80]. When the temperature region of the nucleation is sufficiently below that of the growth, so that the TA peak is taken as the growth process of preexisting nuclei, the kinetic model for the growth changes with the concentration of the nuclei. Assuming a constant-rate nucleation during the temperature region of nucleation from T_1 to T_2 , the number of nuclei per unit volume N is inversely proportional to the heating rate ϕ applied [81]

$$N = \frac{1}{\phi} \int_{T_1}^{T_2} v_n dT = \frac{N_0}{\phi} \quad (18)$$

where v_n is the nucleation rate which is constant irrespective of temperature and N_0 is consequently a constant. Assuming the linear law of the linear growth rate at a constant temperature, the fractional crystallization α is expressed by

$$\alpha = \frac{\delta}{V_0} N k_g(T)^\lambda t^\lambda \quad (19)$$

where $\alpha = V(t)/V_\infty$, δ is a shape index, λ is the growth dimension, and $k_g(T)$ is a rate constant of linear growth. By considering the effects of nuclear overlapping and ingestion, the following equation has been derived by Avrami [82]

$$d\alpha_E = \frac{d\alpha}{1 - \alpha} \quad (20)$$

where α_E is so-called “extended” fractional conversion. Hence

$$\alpha_E = \int_0^t \frac{d\alpha}{1 - \alpha} = -\ln(1 - \alpha) \quad (21)$$

Combining Eqs. (19) and (21), we obtain

$$-\ln(1 - \alpha) = \frac{\delta N}{V_\infty} k_g(T)^\lambda t^\lambda \quad (22)$$

Taking into account the change in the concentration of nuclei, Eq. (22) becomes

$$[-\ln(1 - \alpha)]^{1/\lambda} = \left(\frac{\delta N_0}{\phi V_0} \right)^{1/\lambda} k_g(T) t = k_{app} t \quad (23)$$

Assuming the Arrhenius temperature dependence of $k_g(T)$, the temperature dependence of k_{app} is expressed by

$$k_{app} = \left(\frac{\delta N_0}{\phi V_0} \right)^{1/\lambda} A \exp\left(-\frac{E}{RT}\right) = A_{app} \exp\left(-\frac{E}{RT}\right) \quad (24)$$

Accordingly, the value of A_{app} is dependent on ϕ and V_0 . Thus, reductions in ϕ and V_0 are required to obtain the specific kinetic parameters.

When the temperature increases at a constant heating rate ϕ during the nucleation and growth process, the following kinetic equation is obtained

$$-\ln(1 - \alpha) = \frac{\delta N_0}{\phi V_0} \left[\frac{A}{\phi} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \right]^\lambda \quad (25)$$

Using an approximation of the temperature integral, Eq. (25) is rewritten as

$$-\ln(1 - \alpha) = \frac{\delta N_0 A^\lambda}{\phi^{\lambda+1} V_0} \left[\frac{E \exp(-x)}{R x} \pi(x) \right]^\lambda \quad (26)$$

where $x = E/RT$. The practical kinetic equation for such a crystallization process was originally derived by Matsushita and Sakka [83] as a modified form of the Kissinger equation [84]

$$\ln \frac{\phi^{\lambda+1}}{T_p^2} = -\frac{\lambda E}{RT_p} + \text{const.} \quad (27)$$

where T_p is the maximum of the TA peak. If such a crystallization process is analyzed kinetically using the original Kissinger method, the E_{app} is distorted from the true value of E according to the equation [85]

$$E_{app} = \frac{\lambda E + 2\lambda RT_p}{\lambda + 1} \quad (28)$$

The complex process of nucleation and growth kinetics was treated in detail by Kemeny and Šesták [86].

3. Discussion

TA curves for various types of solid-state reactions have been the bases of kinetic calculations. The accuracy of the calculation methods derived from the general kinetic equation (Eq. (3)), modified by integration or derivation, has been confirmed by theoretically drawn TA curves, showing rather precise correspondence to the kinetic parameters assumed. In practice, however, the accuracy of the calculation methods is not always preserved, because the preliminary requisite of the kinetic equation employed is not always satisfied by the experimentally resolved TA curves. Although the precise measurement of temperature is always required for a better thermal analysis [26], the reliability of the TA data as a possible source of the kinetic curve is influenced by the nature of the reaction under investigation and by the sample and measuring conditions, which are selected depending on the purpose

of kinetic study. In this sense, the kinetic procedure must include a check system for the reliability of the TA curves, in addition to the reliability of the TA instrument and/or measurement. A simple example is the examination of the experimental temperature conditions during the course of a reaction, because the programmed temperature condition is more or less distorted by the self-cooling and/or self-heating of the reaction [87,88].

The method of kinetic calculation has to be selected on the basis of the reliability of the TA curves examined in drawing kinetic curves, in the light of the limitation of the kinetic method. On evaluating the kinetic parameters, the respective calculation method itself can be used to check the prerequisite of the kinetic calculation. Isoconversion methods provide the range of α in which the values of E_{app} remain constant. Although, in many cases, the resultant Arrhenius parameters are dependent on the working temperature interval as described above, the single-run method is useful for evaluating the range of heating rates in which the kinetic obedience remains unchanged. These are the measures of the “isokinetic hypothesis” among various runs at different heating rates during the restricted range of α . Further determination of the kinetic parameters is possible only on the basis of a constant, thus characteristic, value of E_{app} and the “isokinetic hypothesis”. To extend the range of kinetic calculation, it is required to modify the general kinetic equation and/or to formulate a new kinetic equation by taking into account the factors disturbing the “isokinetic hypothesis”. It is necessary to pay close attention to determining the appropriate kinetic model function, because the inappropriate kinetic model function disturbs the reliable determination of the Arrhenius parameters as described above. The kinetic model function has to be extended, if necessary, from the conventional physico-geometric models to the more sophisticated empirical models [72,73,76,89,90]. On determining the pre-exponential factor, it should be considered that the constant value of A_{app} at different α values within the α range of the kinetic calculation is also a prerequisite for the applicability of Eq. (3), as is the case of the E_{app} values. In addition, the constant value of A_{app} is obtained only when the appropriate kinetic model function is used. The constancy of A_{app} at different α can also be a check for the applicability of the kinetic procedure employed.

The kinetic parameters thus determined will be used for the comparative study of a series of solid-state reactions. Although the purpose of the kinetic study is to characterize the kinetic process using the kinetic parameters which are the process constants, it is necessary here to check the variation of the Arrhenius parameters dependent on the working temperature interval ΔT . Because the linear correlation of the apparent Arrhenius parameters with ΔT is taken as a simple mathematical consequence of the exponential form of the general kinetic equation (see above), in such a case it is not expected to interpret the variation in the apparent Arrhenius parameters on the basis of physico-chemistry alone. The correlation analysis, including the physico-chemical interpretation of the KCE, is only interesting for kinetic parameters that have been checked carefully in the manner described above.

Fig. 7 shows a flow chart of the kinetic procedure including the check system. It seems that the checking process itself has a kinetic significance and serves as an

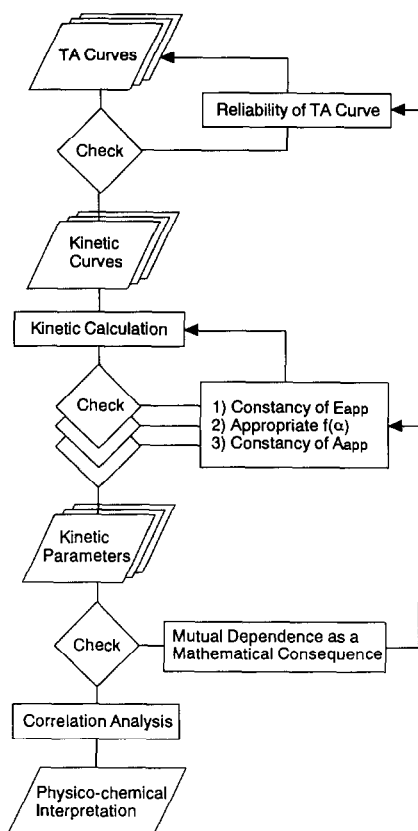


Fig. 7. A flow chart of the kinetic procedure including the check system.

evaluation of the meaningful kinetic parameters, because any method of the kinetic calculation cannot accommodate the widely distributed original TA curves which depend on the type of TA instrument, the nature of the reaction processes and the experimental factors [90]. In obtaining reliable TA kinetics it is desirable to establish a check system for the standard kinetic procedure and to report the checking process in the respective kinetic papers.

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