

Data Treatment in Non-isothermal Kinetics and Diagnostic Limits of Phenomenological Models

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Kinetic models of solid-state reactions are often based on a formal description of geometrically well defined bodies treated under strictly isothermal conditions; for real processes these assumptions are evidently incorrect. The kinetic parameters are distorted by the difference of the real process from the idealized kinetic model. In this respect, it can be useful to find an empirical function containing the smallest possible number of constants, so that there is some flexibility enough to describe real process as closely as possible. In such a case the models of heterogeneous kinetics can be assumed as a distorted case of the simpler homogeneous kinetics and then mathematically treated by multiplying an "accommodation" function. The empirical function also accommodates the deviation of the non-isothermal process from the process under the isothermal condition. The mutual dependence of the Arrhenius parameters observed empirically is recognized as a simple mathematical consequence of the exponential form of the rate constant in the Arrhenius equation, resulting from both the poorly controlled measuring condition in the thermal analysis and the false kinetic treatment. The isoconversion method allows to check the invariance of the activation energy during the course of reaction, which is the fundamental assumption in the derivation of the kinetic equation. Once the characteristic activation energy is determined, it is possible to find the kinetic model function which best describes the measured set of TA data using the two special functional relationships in the kinetic equation.

Introduction

In contradiction to the well established spot measurements frequently employed to investigate solid-state reactions, although affected by inadequate

freeze-in and poor localization of the reaction, the centered measurements of a property representing the average state of a sample are often considered less convenient due to superstitiously bad reputation of its mere phenomenological character. The latter

group is represented by methods of thermal analysis (TA) carried out under constant heating and/or cooling. TA curves are often treated in terms of homogeneous-like kinetic description yielding non-integral values of reaction orders which are almost meaningless in heterogeneous kinetics. However, even the homogeneous reactions exhibiting nonrandomness of the reactant distribution and/or diffusion controlled subprocess can be described by reactions on fractal domains, the hallmark being the anomalous reaction orders. It is clear that the present state-of-art of the thermoanalytical kinetics¹⁾ as applied to heterogeneous reactions is not appropriate to sophisticated means available in solid-state chemistry, the linkage of most treatments to the traditional geometrical description being very firm and hard to overcome¹⁻³⁾. The use of phenomenological models has been criticized²⁾ but a unified approach is still missing as well as the correlation between the microscopic process (detectable only locally under not well guaranteed conditions) and macroscopic process (capable of measuring in situ even at changing temperatures). With gradual increment of complexity of an experimentally resolved kinetic curve from TA measurement of the reaction investigated, the kinetic approach tends to be mere distinguishment of the proportional relevancy of the individual groups of phenomenological models. Important is the discussion on the applicability and limitation of the kinetic analysis of non-isothermal data.

In this article, the present orthodoxy of the kinetic study of the solid-state reactions by means of TA is reviewed briefly. Some problems, resulting from the distortion of the real reaction process detected by TA measurements from the ideal case assumed to formulate the kinetic equation, are pointed out in connection with some consequence of the mutual correlation of the kinetic parameters and their implications for a reliable kinetic analysis. A possible way to accommodate such a deviation in the kinetic equation is discussed by introducing the accommodation function $a(\alpha)$ ⁴⁾. The significance of an empirical kinetic model function known as the Sestak-Berggren (SB) model is investigated in relation to $a(\alpha)$. Taking account of these findings,

two types of mathematical relationships useful to characterize the kinetics are reviewed.

The Kinetic Equation

Assuming the kinetic model function $f(\alpha)$ and the Arrhenius type of temperature dependence of the rate constant, the following equation is applied for analyzing kinetically the TA curves of the solid-state reaction³⁾.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where A and E are the Arrhenius parameters and α is the fractional conversion. The kinetic model function $f(\alpha)$ is derived on the basis of physico-geometric assumptions on the movement of reaction interface. Figure 1 represents a schematic diagram of a hypothetical transfer of the geometry of the system from the dimensionless homogeneous-like model to the idealized heterogeneous model by introduction of dimensionality. It is important to recall that character of kinetic description drastically changes from the concentration dependent (homogeneous) to that of the interface-to-volume dependent (heterogeneous). The mathematical formulae of the commonly cited $f(\alpha)$ are summarized in Table 1.

Because the rate constant is characteristic for the $f(\alpha)$ assumed, the Arrhenius parameters are mutually correlated with the $f(\alpha)$. As a simple mathematical consequence of the exponential form of the rate constant, the distortion of the Arrhenius parameters by the inappropriate kinetic model function is expressed by⁵⁾

$$\frac{E_{app}}{E} = \frac{f(\alpha_p)F'(\alpha_p)}{F(\alpha_p)f'(\alpha_p)} \quad (2)$$

with $f'(\alpha) = df(\alpha)/d\alpha$ and $F'(\alpha) = dF(\alpha)/d\alpha$, and

$$\ln \frac{A_{app}}{A} = \frac{E}{RT_p} \left[\frac{f(\alpha_p)F'(\alpha_p) - F(\alpha_p)f'(\alpha_p)}{F(\alpha_p)f'(\alpha_p)} \right] + \ln \frac{f(\alpha_p)}{F(\alpha_p)} \quad (3)$$

where E_{app} and A_{app} are the apparent Arrhenius parameters distorted by the use of an inappropriate model $F(\alpha)$ instead of the appropriate one $f(\alpha)$. The subscript p indicates the values correspond to the

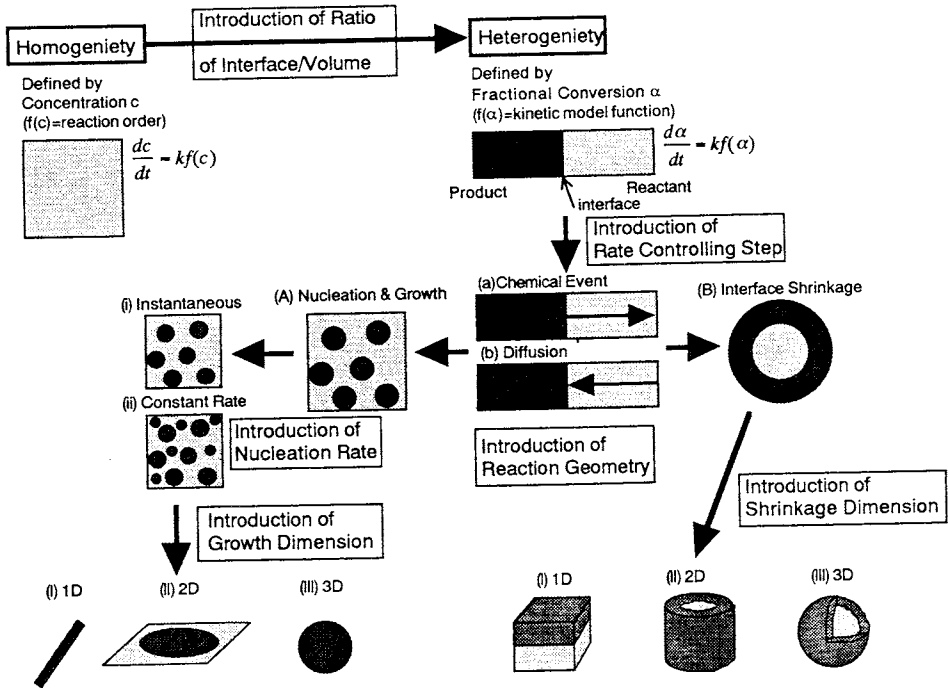


Fig.1 Schematic diagram of a hypothetical transfer of the system geometry from the non-dimensional homogeneous-like model to the idealized heterogeneous model by introduction of dimensionality, due to the interface formation and interface growth.

Table 1 The kinetic model functions $f(\alpha)$ usually employed for the kinetic analysis of the solid-state reaction, together with their integral $g(\alpha)$ and differential $f'(\alpha)$ forms.

Model	Symbol	$f(\alpha)$	$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$	$f'(\alpha) = \frac{f(\alpha)}{d\alpha}$
Nucleation & Growth (Avrami-Erofeev)	A_m ($m = 0.5, 1, 1.5, 2, 2.5, 3$ and 4)	$m(1-\alpha)[- \ln(1-\alpha)]^{-1/m}$	$[- \ln(1-\alpha)]^{1/m}$	$\frac{m-1}{[- \ln(1-\alpha)]^{1/m}} - \frac{m}{[- \ln(1-\alpha)]^{1/m-1}}$
Phase Boundary Controlled Reaction	R_n ($n = 1, 2$ and 3)	$n(1-\alpha)^{1-1/n}$	$1 - (1-\alpha)^{1/n}$	$-\frac{n-1}{(1-\alpha)^{1/n}}$
One-dimensional Diffusion	D_1	$\frac{2}{\alpha}$	α^2	$-\frac{2}{\alpha^2}$
Two-dimensional Diffusion	D_2	$-\frac{1}{\ln(1-\alpha)}$	$\alpha + (1-\alpha)\ln(1-\alpha)$	$-\frac{1}{(1-\alpha)[\ln(1-\alpha)]^2}$
Three-dimensional Diffusion (Jander)	D_3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$	$[1-(1-\alpha)^{1/3}]^2$	$\frac{1/2 - (1-\alpha)^{-1/3}}{[1-(1-\alpha)^{1/3}]^2}$
Three-dimensional Diffusion (Ginsting-Brounshtein)	D_4	$\frac{3}{2[(1-\alpha)^{-1/3} - 1]}$	$1 - \frac{2\alpha}{3} - (1-\alpha)^{2/3}$	$-\frac{1}{2(1-\alpha)^{4/3}[(1-\alpha)^{-1/3} - 1]^2}$

maximum of the TA peak.

In practice, if the reaction order $RO(N)$ model, $(1-\alpha)^N$, was used instead of the appropriate kinetic model function $f(\alpha)$, the ratio of the apparent and the true activation energies E_{app}/E can be expressed by the following equation⁵⁾:

$$\frac{E_{app}}{E} = - \left(\frac{f(\alpha_p)}{f'(\alpha_p)} \right) \frac{N_{app}}{1 - \alpha_p} \quad (4)$$

where N_{app} is an apparent kinetic exponent of the $RO(N)$ model. The value of N_{app} is characteristic for the $f(\alpha)$ but α_p depends also on the $x_p = E/RT_p$. Therefore the value of E_{app}/E slightly increases with increasing x_p for the $f(\alpha)$ of diffusion controlled models⁶⁾. On the other hand, the E_{app}/E ratio decreases with increasing x_p for the A_m model according to the equation⁷⁾:

$$\frac{E_{app}}{E} = \frac{m-1}{x_p \pi(x_p)} + 1 \quad (5)$$

where m is the true kinetic exponent of the A_m model and $\pi(x)$ is the approximation of the temperature integral³⁾.

It should be emphasized that many workers are concerned with the kinetic analysis of a single TA curve. However, the methods are somewhat problematic because of the apparent kinetic models. For example the popular Freeman and Carroll method⁸⁾ was derived for the $RO(N)$ model. Therefore, this method always gives apparent parameters N_{app} and E_{app} corresponding to the $RO(N)$ model regardless of the true kinetic model. Similarly it must be borne in mind, that the non-linear or multiple linear regression methods can lead to incorrect results because any TA curve can be interpreted within the scope of the $RO(N)$ model depending on the value of apparent activation energy.

Accommodation Function and Empirical Kinetic Model

Figure 2 represent a typical polarizing microscopic view of internal surfaces of partially dehydrated crushed crystals of $K_2CuCl_4 \cdot 2H_2O$. The irregularly shaped sample particles and reaction interfaces are apparently different from the idealized $f(\alpha)$. In

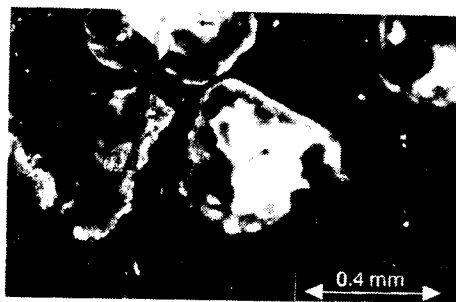


Fig.2 Typical polarizing microscopic view of the internal surface of the partially dehydrated crushed crystals of $K_2CuCl_4 \cdot 2H_2O$.

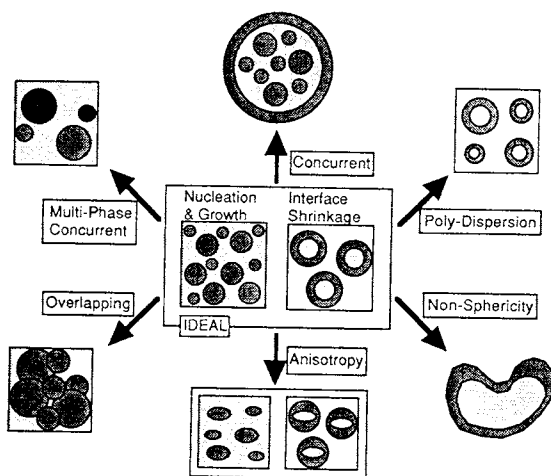


Fig.3 Schematic diagram of the practical reaction processes.

addition, the behavior of real particles does require to account for polydispersity, shielding and overlapping, unequal mixing, anisotropy and so on, as is shown schematically in Fig.3. The kinetic model functions $f(\alpha)$ derived on the basis of physico-geometric assumptions of regularly shaped bodies evidently can hardly describe such a real heterogeneous system which we have to take into consideration. The disagreement between the idealized process, assumed in formulating the $f(\alpha)$, and the actual process, investigated as an averaged phenomena by the TA measurements, leads to the distortion of the Arrhenius parameters according to eqns. (2) and (3).

Table 2 The kinetic model functions $h(\alpha)$ with the non-integral kinetic exponent and the accommodation function $a(\alpha)$, together with their physico-chemical meanings.

$f(\alpha)$	Kinetic exponent of interface advancement	Dimensionality	Kinetic exponent of nucleation	$h(\alpha)$	$a(\alpha)$
R_n	1	fractal value N	---	$N(1-\alpha)^{-1/N}$	$\frac{N}{n}(1-\alpha)^{(N-n)/nN}$
R_3	non-integral value p	3	---	$\frac{3(1-\alpha)^{2/3}}{p[1-(1-\alpha)^{1/3}]^{p-1}}$	$\frac{1}{p[1-(1-\alpha)^{1/3}]^{p-1}}$
R_n	non-integral value p	fractal value N	---	$\frac{N(1-\alpha)^{-1/N}}{p[1-(1-\alpha)^{1/N}]^{p-1}}$	$\frac{N(1-\alpha)^{(N-n)/nN}}{n p[1-(1-\alpha)^{1/N}]^{p-1}}$
D_3	2	fractal value N	---	$\frac{N(1-\alpha)^{-1/N}}{2[1-(1-\alpha)^{1/N}]}$	$\frac{N}{3}(1-\alpha)^{(N-3)/3N}$
A_m	non-integral value	fractal value	non-integral value	$M(1-\alpha)[- \ln(1-\alpha)]^{1-1/M}$	$\frac{M}{m}[- \ln(1-\alpha)]^{(M-n)/mM}$

Introducing the accommodation function $a(\alpha)$, the discrepancy of the idealized $f(\alpha)$ from the actual kinetic model function $h(\alpha)$ can be expressed as⁴⁾:

$$h(\alpha) = f(\alpha)a(\alpha) \tag{6}$$

Then the kinetic expression $h(\alpha)$ can be regarded as the distorted case of the homogeneous-like kinetics and of $f(\alpha)$, with a possible $a(\alpha)$ to decrease the difference of the idealized $f(\alpha)$ from the practical process. Mathematical formalism of the $a(\alpha)$ is possible for a certain case. The simplest example of the accommodation is the application of the non-integral kinetic exponents into the $f(\alpha)$. Table 2 lists the form of $a(\alpha)$ for the $h(\alpha)$ having the non-integral exponents, together with their physico-geometric meaning⁹⁾. Although the reaction geometry is also influenced by the extensive factors, from the simple geometric consideration the non-integral exponent is taken as the value corresponding fractal dimension¹⁰⁾.

It is apparent, however, that the accommodation of the more complicated process in the $h(\alpha)$ is extremely difficult based on the real physical chemistry and is possibly expressed by the empirical (analytical) formula. The validity of procedures and resulting functions in deriving kinetic models in question was approved also for non-isothermal

conditions elsewhere^{11),12)}. From this point of view it would be useful to find an empirical function $h(\alpha)$ containing the smallest possible number of constants, so that there is some flexibility enough to describe real TA data as closely as possible³⁾. Twenty years ago, Sestak and Berggren¹³⁾ proposed an empirical kinetic model in the form

$$h(\alpha) = \alpha^m(1-\alpha)^n[- \ln(1-\alpha)]^l \tag{7}$$

It was believed^{2),3)} that this kinetic equation, containing as many as three exponential terms, is able to describe any TA curves. Further mathematical analysis¹⁴⁾ of eqn. (7) has shown, however, that no more than two kinetic exponents are necessary. Therefore, after eliminating the third exponential term in eqn. (7) the final form obtained is

$$h(\alpha) = \alpha^m(1-\alpha)^n \tag{8}$$

In the literature the eqn. (8) is cited as the Sestak Berggren $SB(m,n)$ kinetic model. Exponents m and n are taken as kinetic parameters which describe the shape of measured TA curves. The SB model, eqn. (7), can also be understood in terms of the $a(\alpha)$, where $a(\alpha)$ can bear the form of either function, α^m , $(1-\alpha)^{1-n}$ and/or $[- \ln(1-\alpha)]^l$. It serves particularly to fit the prolonged reaction tails due to the actual

Table 3 Typical empirical kinetic model functions $h(\alpha)$, together with their integral form $G(\alpha)$ and differential form $h'(\alpha)$.

Type	Symbol	$h(\alpha)$	$G(\alpha) = \int_0^\alpha \frac{d\alpha}{h(\alpha)}$	$h'(\alpha) = \frac{h(\alpha)}{d\alpha}$
Reaction order	$RO(N)$	$(1-\alpha)^N$	$\frac{1-(1-\alpha)^{1-N}}{1-N}$	$-N(1-\alpha)^{N-1}$
Johnson-Mehl-Avrami-Erofeyev	$JMA(M)$	$M(1-\alpha)[- \ln(1-\alpha)]^{1-1/M}$	$[- \ln(1-\alpha)]^{1/M}$	$\frac{M-1}{[- \ln(1-\alpha)]^{1/M}} - \frac{M}{[- \ln(1-\alpha)]^{1/M-1}}$
Sestak-Berggren	$SB(m,n)$	$\alpha^m(1-\alpha)^n$	no analytical form	$m\alpha^{m-1}(1-\alpha)^n - n\alpha^m(1-\alpha)^{n-1}$

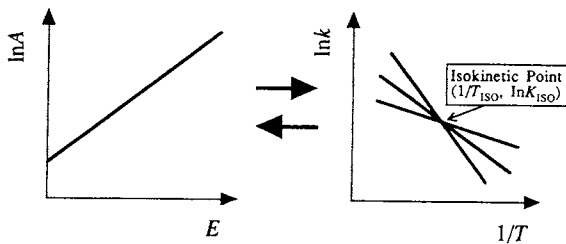


Fig.4 Schematic representation of the mutual dependence of the Arrhenius parameters.

behavior of real particles and can match the particle non-sphericity in view of the morphology description in terms of the characteristic dimensions (usually the longest particle length), interface (the average boundary line) and volume (the mean section area). Table 3 lists the typical empirical model $h(\alpha)$, together with their integral and differential forms.

Correlation of the Arrhenius Parameters

It is rather an empirical fact that both the activation energy and preexponential factor in eqn. (1) are mutually correlated known as the kinetic compensation effect (KCE)¹⁵⁾. This correlation can be expressed by the following equation.

$$\ln A = a + bE \tag{9}$$

where a and b are constants. Any change in the activation energy is therefore "compensated" by the change of $\ln A$ as expressed by eqn.(9). The simple relationship of eqn. (9) can be derived as a mathematical consequence of the exponential form of the rate constant in the Arrhenius equation¹⁶⁾ and seems to arise from a projection of the interrelationship among $\ln A$, E and temperature, T , terms to the $\ln A$ vs. E coordinate¹⁷⁾, see Fig.4. From this point of view, the KCE can be divided into two categories according to whether the KCE is accompanied by changes in the temperature interval analyzed or not¹⁸⁾.

As described in the previous section, the KCE arising from a single non-isothermal TA curve by the use of various inappropriate kinetic model

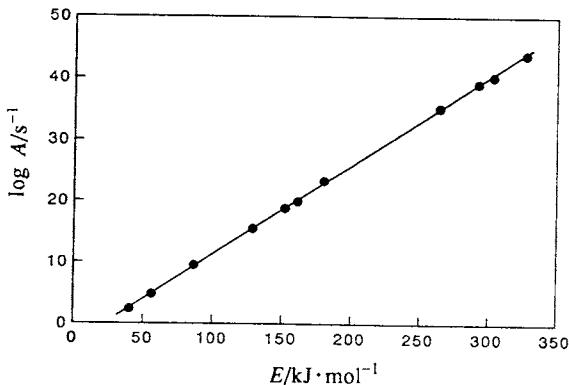


Fig.5 The kinetic compensation behavior of the apparent Arrhenius parameters obtained using various inappropriate $f(\alpha)$ for a theoretical curve drawn by assuming $E=150$ kJ/mol, $\log A=18.5$ 1/s, Heating Rate=0.5 K/min and the R_2 law.

functions is one of the examples where the T terms remain constant⁵⁾. As an example, Figure 5 shows the KCE behavior of the apparent Arrhenius parameters obtained using various inappropriate $f(\alpha)$ for a theoretical curve drawn by assuming $E=150$ kJ/mol, $\log A=18.5$ 1/s, Heating Rate=0.5 K/min and R_2 law. It seems, therefore, problematic to obtain all the kinetic parameters from only one experimental TA curve. Similarly, we have to realize that this problem cannot be solved even using the most sophisticated non-linear regression algorithms unless the kinetic model or at least one kinetic parameter is a *priori* known.

On the other hand, in the case of a KCE established between the Arrhenius parameters obtained from more than one TA curve under various sample and measuring conditions, the changes in the values of E and $\ln A$ are always accompanied by a change in the working temperature interval of kinetic analysis¹⁹⁾. For the values of E_{app} and A_{app} , the following relationships can be derived by using the lowest temperature, T_L , the highest temperature, T_H , and $\Delta T=T_H-T_L$

$$E_{app} = \frac{RT_H T_L}{\Delta T} \ln X \quad (10)$$

$$\ln A_{app} = \frac{1}{T_{iso}} \frac{T_H T_L}{\Delta T} \ln X + \ln k_{iso} \quad (11)$$

where X depends on the calculation method. Table 4 lists the form of X for the respective method of kinetic calculation. The variation in the value of $\ln X$ due to the different reaction temperatures is relatively small compared with the change in the value of $T_H T_L / \Delta T$. This implies that a constant value of $T_H T_L / \Delta T$ is a necessary condition for obtaining a constant E_{app} value²⁰⁾. In this case, however, a constant value of $\ln A$ is not necessarily obtained; the constant value of ΔT can yield constant Arrhenius parameters. This is explained that, for a smaller ΔT , even the change in $T_H T_L$ can be ignored in comparison with the change in $1/\Delta T$. When the KCE is established among several sets of Arrhenius parameters, the values of E_{app} and $\ln A_{app}$ are to be a function of $1/\Delta T$. Figure 6 represents the practical example of the $1/\Delta T$ dependence of the apparent E values obtained at different α for the nonisothermal dehydration of single crystalline $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

Such a change in the working temperature interval, which is not expected from the present orthodoxy of kinetic analysis, seems to be due to both the deviation of the apparent reaction condition from the idealized measuring conditions and the changes in the reaction process with the sample and measuring conditions. The gradients in the temperature and gaseous pressure and these continuous changes during the course of reaction are

Table 4 The mathematical form of X in eqns. (10) and (11) for the respective method of kinetic calculation.

Method	X^*
Isothermal methods	$\frac{(d\alpha/dt)_H}{(d\alpha/dt)_L}$
Non-isothermal single run methods	$\frac{(d\alpha/dT)_H f(\alpha_L)}{(d\alpha/dT)_L f(\alpha_H)}$
Non-isothermal isoconversion methods	$\frac{(d\alpha/dT)_H \beta_H}{(d\alpha/dT)_L \beta_L}$
Non-isothermal peak methods	$\frac{f'(\alpha_L) T_L^2 \beta_H}{f'(\alpha_H) T_H^2 \beta_L}$

* β is the heating rate and the subscripts H and L indicate the highest and lowest values, respectively.

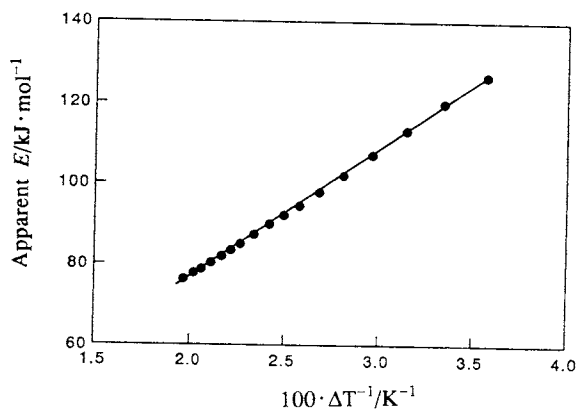


Fig.6 The $1/\Delta T$ dependence of the apparent E values obtained at different α for the non-isothermal dehydration of single crystalline $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

likely to be the important causes of the former²¹⁾⁻²³⁾. In this sense, the Controlled Transformation rate Thermal Analysis (CRTA)²⁴⁾ has a merit, because the self-generated condition remains constant during the reaction, at least, compared with the traditional isothermal and non-isothermal measurements²⁵⁾⁻²⁷⁾. The latter is the case where the apparent Arrhenius parameters are related to several elementary processes²⁸⁾, *i.e.*, nucleation, interface chemical reaction and diffusion, which became particularly important in the analysis of the crystallization processes such as molten polymer^{29),30)} and quenched glasses³¹⁾⁻³³⁾. Any gradual change in the reaction mechanism and/or the rate limiting step during the reaction is also responsible for the change in the kinetic parameters with α ³⁴⁾⁻³⁶⁾.

The Kinetic Analysis

The correlation of the kinetic parameters with the apparent kinetic models does not allow to perform correctly the kinetic analysis using only one experimental TA curve. This problem can be solved, however, if the true activation energy is known. Then the most probable kinetic model can be determined and subsequently the preexponential term is calculated. The method of kinetic analysis is described in the following sections.

Calculation of the Activation Energy

The calculation of activation energy is based on

multiple scan methods where several measurements at different heating rates are required, *i.e.*, the isoconversion methods³⁷⁾. Logically the isoconversion methods can be divided into the Ozawa-Flynn-Wall method^{38),39)}, the Kissinger-Akahira-Sunose method⁴⁰⁾ and the expanded Friedman method^{41),42)}. These methods allow to check the invariance of E with respect to α which is one of the basic assumptions in the kinetic analysis⁴³⁾.

Among others, the expanded Friedman method has the wider applicability⁴²⁾. Taking logarithms of eqn.(1)

$$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E}{RT} \quad (12)$$

The slope of $\ln(d\alpha/dt)$ vs. $1/T$ for a given value of α gives the activation energy. The applicability of eqn.(12) can be estimated by introducing the generalized time θ ⁴⁴⁾:

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (13)$$

First differentiation gives

$$\frac{d\theta}{dt} = \exp\left(-\frac{E}{RT}\right) \quad (14)$$

Combining eqn.(1) with eqn.(14),

$$\frac{d\alpha}{d\theta} = Af(\alpha) \quad (15)$$

Eqn.(1) is thus expressed by

$$\frac{d\alpha}{dt} = \frac{d\alpha}{d\theta} \frac{d\theta}{dt} \quad (16)$$

Eqns. (14) and (16) show that $d\alpha/dt$ is proportional to $\exp(-E/RT)$ at a given α , having the proportional constant of $d\alpha/d\theta$. Since eqns.(14), (15) and (16) hold for any temperature change, eqn.(12) can be applied to any TA data obtained under any condition of temperature change⁴²⁾. Thus eqn.(12) can successfully be used for the TA curves even if the programmed temperature condition was distorted by the self-cooling and/or self-heating as well as for the CRTA curves⁴⁵⁾.

Determination of the Kinetic Model

Once the activation energy has been determined we can find the kinetic model which best describes a measured set of TA data. Malek⁷⁾ has shown that for this purpose it is useful to define two special functions $y(\alpha)$ and $z(\alpha)$ which can easily be obtained by simple transformation of experimental data.

Through rearrangement of eqn.(1), the function $y(\alpha)$ is defined as⁴⁶⁾:

$$y(\alpha) = \frac{d\alpha}{dt} \exp\left(-\frac{E}{RT}\right) = Af(\alpha) \quad (17)$$

The $y(\alpha)$ function corresponds to $d\alpha/d\theta$ and is proportional to the $f(\alpha)$ function. Thus by plotting $y(\alpha)$ dependence, normalized within $\langle 0,1 \rangle$ interval, the shape of function $f(\alpha)$ is obtained. The $y(\alpha)$ function is, therefore, characteristic for a given kinetic model $f(\alpha)$ and it can be used as a diagnostic tool for the kinetic model determination. The mathematical condition for the maximum of the $y(\alpha)$ function can be written as:

$$f'(\alpha) = -\frac{df(\alpha)}{d\alpha} = 0 \quad (18)$$

Comparing eqn.(18) with the different form of the respective $f(\alpha)$ (see Table 1), the D_1, D_2, D_3, D_4 and R_n models have a maximum at $\alpha_M=0$. On the other hand, the $JMA(M)$ and $SB(m,n)$ models have a maximum at $0 < \alpha_M < \alpha_p$. For the $JMA(M)$ model, the relationship between the α_M value and kinetic exponent M is represented as:

$$\alpha_M = 1 - \exp\left(\frac{1-M}{M}\right) \quad (19)$$

It is written for the $SB(m,n)$ model as:

$$\alpha_M = \frac{m}{m+n} \quad (20)$$

Figure 7 shows schematically the character of the $y(\alpha)$ function with respect to various kinetic model functions. It should be stressed that the shape of the $y(\alpha)$ function is strongly affected by E . Hence the true activation energy is decisive for a reliable determination of the kinetic model because of the correlation of kinetic parameters.

Similarly, we can discuss the mathematical

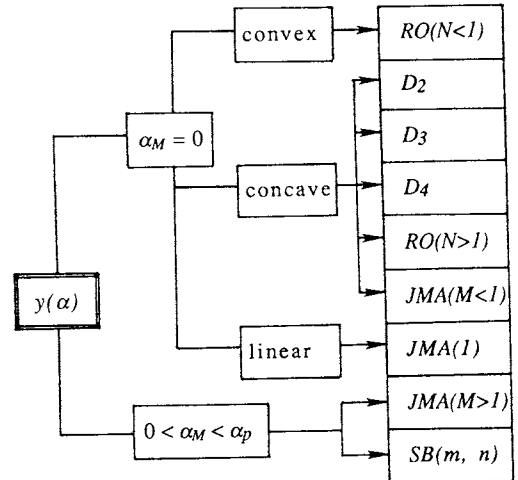


Fig.7 Schematic diagram of the kinetic model determination by using the $y(\alpha)$ function.

properties of the $z(\alpha)$ function. If the temperature rises at a constant rate β , integration of eqn.(1) gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{\beta R} \exp(-x) \left[\frac{\pi(x)}{x} \right] \quad (21)$$

By combining eqns.(1) and (21), an alternative kinetic equation is obtained:

$$\frac{d\alpha}{dt} = \left[\frac{\beta}{T\pi(x)} \right] f(\alpha)g(\alpha) \quad (22)$$

After rearrangement of eqn.(22), the $z(\alpha)$ function is defined as⁴⁷⁾:

$$z(\alpha) = \pi(x) \frac{d\alpha}{dt} \frac{T}{\beta} = f(\alpha)g(\alpha) \quad (23)$$

Differentiation of eqn.(23) with respect to α gives:

$$z'(\alpha) = f'(\alpha)g(\alpha) + 1 \quad (24)$$

In addition, by differentiating eqn.(22)⁴⁸⁾:

$$\left(\frac{d^2\alpha}{dt^2} \right) = \left[\frac{\beta}{T\pi(x)} \right]^2 f(\alpha)g(\alpha) [f'(\alpha)g(\alpha) + \pi(x)] \quad (25)$$

By setting eqn.(25) equal to zero, the mathematical condition for the maximum of TA peak is obtained:

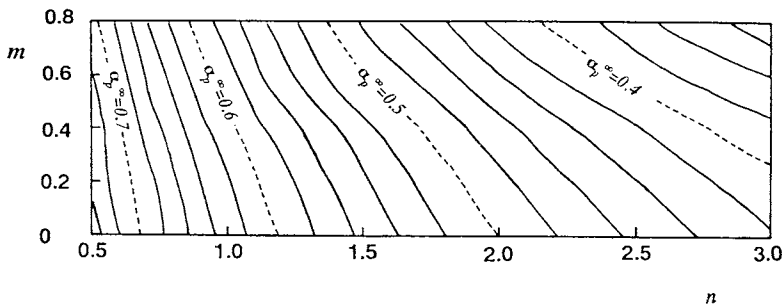


Fig.8 The dependence of the maximum of the $z(\alpha)$ function α_p^∞ on the kinetic exponents for the $SB(m,n)$ kinetic model.

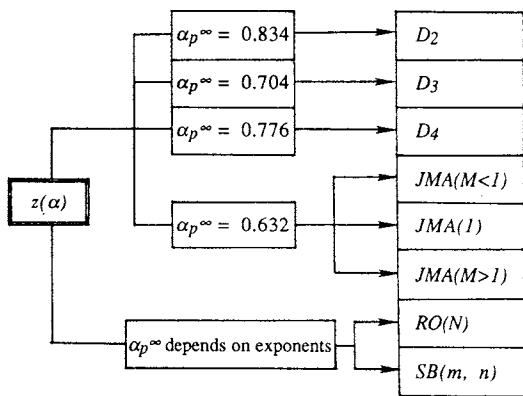


Fig.9 Schematic diagram of the kinetic model determination by using the $z(\alpha)$ function.

$$-f'(\alpha_p)g(\alpha_p) = x_p \pi(x_p) \tag{26}$$

When x_p is infinite, eqn.(26) is written as:

$$-f'(\alpha_p^\infty)g(\alpha_p^\infty) = \lim_{x_p \rightarrow \infty} [x_p \pi(x_p)] = 1 \tag{27}$$

where α_p^∞ is the α_p at $x_p \rightarrow \infty$. Comparing eqn.(24) with eqn.(27), it is apparent that at the maximum of the $z(\alpha)$ function eqn.(24) sets equal to zero being fulfilled by α_p^∞ . The $z(\alpha)$ function has a maximum at α_p^∞ for all kinetic models summarized in Table 1, having the characteristic value of α_p^∞ for respective kinetic models. It is interesting that the α_p^∞ value practically does not depend on the value of activation energy used to calculate $z(\alpha)$ (in fact it varies within 1% of the theoretical value). An important fact is that the α_p^∞ is invariant with respect to the kinetic exponent for the $JMA(M)$

model. On the other hand for both the $RO(N)$ and $SB(m,n)$ models the parameter α_p^∞ depends on the values of kinetic exponents as shown in Fig. 8. Figure 9 shows schematically the property of $z(\alpha)$ function for the respective kinetic model function.

It is evident that the shape of the $y(\alpha)$ function as well as the maximum α_p^∞ of the $z(\alpha)$ function can be used as a guide to select the kinetic model. Table 5 summarizes the property of $y(\alpha)$ and the value of α_p^∞ for the respective $f(\alpha)$. Both α_M and α_p^∞ parameters are especially useful in this respect. Their combination allows the determination of the most suitable kinetic model as shown by the scheme in Figs. 7 and 9. As we can see, the empirical $SB(m,n)$ model gives the best description of TA data if $\alpha_p^\infty \neq 0.632$ and $\alpha_M \in (0, \alpha_p)$. According to our experience these conditions are fulfilled for some solid-state processes^{49),50)}.

Calculation of Kinetic Exponents

Once the kinetic model is determined the kinetic exponents can be calculated for $RO(N)$, $JMA(M)$ or $SB(m,n)$ model. The calculation method depends on the kinetic model and is described below.

RO(N) model: The kinetic exponent $N \neq 0$ for this model can be calculated iteratively using the equation:

$$\alpha_p = 1 - \left[1 + \frac{1-N}{N} x_p \pi(x_p) \right]^{1/(N-1)} \tag{28}$$

This equation is obtained from eqn.(26) and was derived originally by Gorbachev⁵¹⁾ for a simplified approximation: $\pi(x_p) = 1/(x_p + 2)$

JMA(M) model: If the $y(\alpha)$ function has a maximum

Table 5 The property of the $y(\alpha)$ function and the value of α_p^∞ for the respective kinetic model function.

Model	$y(\alpha)$	α_p^∞
$JMA(M)$	$M < 1$; concave	0.632
	$M = 1$; linear	0.632
	$M > 1$; maximum	0.632
R_2	convex	0.750
R_3	convex	0.704
D_2	concave	0.834
D_3	concave	0.704
D_4	concave	0.776

at $\alpha_M \in (0, \alpha_p)$, i.e. for $M > 1$, then the kinetic exponent M is calculated using the eqn.(19):

$$M = \frac{1}{1 + \ln(1 - \alpha_M)} \quad (29)$$

SB(m,n) model: Rearrangement of eqn.(20) gives the ratio of kinetic exponents $p=m/n$:

$$P = \frac{\alpha_M}{1 - \alpha_M} \quad (30)$$

From the relationship of eqn.(17):

$$\ln y(\alpha) = \ln A + n \ln[\alpha^P(1 - \alpha)] \quad (31)$$

The kinetic parameter n corresponds to the slope of linear dependence of $\ln y(\alpha)$ versus $\ln[\alpha^P(1 - \alpha)]$ for $\alpha \in (0.2, 0.8)$. Then the second kinetic exponent is $m=pn$.

Calculation of the Preexponential Factor

Knowing the value of activation energy and the kinetic model the preexponential factor is calculated. On determining the preexponential factor, it should be considered that the constant value of A at different values of α is also the prerequisite for the application of eqn.(1), as is the case of E . Rearrangement of eqn.(17) gives:

$$A = \frac{y(\alpha)}{f(\alpha)} \quad (32)$$

According to eqn.(32), the value of A at different α can be calculated allowing to check the invariance of A with respect to α .

Alternatively, using the condition of maximum of a TA peak, the preexponential factor is calculated by the following equation^{7),49)}:

$$A = -\frac{\beta x_p}{Tf'(\alpha_p)} \exp(x_p) \quad (33)$$

Software for Kinetic Analysis

It is rather surprising that the distortion of the kinetic parameters by the apparent kinetic model as well as the mutual correlation of the Arrhenius parameters are very often ignored even in the commercially available kinetic software. The experimentally resolved shape of TA curves does not always provide the satisfactory source of kinetic data, because the preliminary requisite of the kinetic equation is not guaranteed during the TA measurement. Although the precise measurement of temperature is always required for a better thermal analysis, the reliability of the TA data is influenced by the nature of reaction under investigation and the sample and measuring conditions are selected depending on the purpose of the kinetic study. Changes in the kinetic parameters for the empirically same reaction may be a simple consequence of trying to describe a complex process by computing the Arrhenius parameters, accepting changes of many order of magnitude of practical reaction condition without question or test⁵²⁾. In this respect, the kinetic software must include the check system of the reliability of the TA curves as a possible kinetic

source. The simple example is the examination of the practical heating rate during the course of reaction, because the programmed heating or cooling rate is distorted by the self-cooling and/or self-heating of the reaction^{22),31)}.

The method of kinetic calculation has to be selected based on the above test of the TA data in the light of the limitation of the kinetic method. Comparison of the kinetic parameters determined using various methods of kinetic calculation provides us with less information on the significance of the kinetic parameters determined. The invariance of the apparent value of E is a measure of the constancy of the reaction mechanism among various runs at different heating rates. Mathematically, the further kinetic analysis is possible only on the basis of the constant, thus characteristic, value of E . In a practical sense, the fluctuation of the value of E diminishes the suitability of the kinetic analysis and regulates the quality of kinetic analysis, *i.e.*, whether it is really physico-chemical or empirical. The acquisition of the most relevant kinetic information from the experimentally resolved TA curves should only be possible on the appropriate level of kinetic analysis⁴⁷⁾.

Taking account of the above discussion, the kinetic software is required to have both the mathematically and practically oriented algorithm including the check system of the kinetic analysis. The checking process itself has a kinetic significance and also serves for the evaluation of meaningful kinetic parameters. Any method of the kinetic calculation cannot accommodate the widely distributed conditions which depend on the type of TA instrument, the nature of reaction processes and the experimental factors.

Conclusion

It was shown that the kinetic exponent in the kinetic model function, the activation energy and the preexponential factor are mutually correlated. As a consequence of this correlation any TA curve can be described by an apparent kinetic model instead of the appropriate one with a certain value of apparent Arrhenius parameters. The use of the conventional kinetic model is sometimes to be a source of the

distortion of the Arrhenius parameters, because the real heterogeneous process detected by TA measurements is hardly to be described by the conventional kinetic model function which is derived based on the geometrically well defined bodies under strictly isothermal condition. The empirical kinetic model, $SB(m,n)$, accommodates the discrepancy of the real process from the idealized process, with the flexibility enough to describe the real process as closely as possible. In terms of the accommodation function $a(\alpha)$, the physico-geometry of the process could also be predicted from the empirical kinetic exponents with non-integral values. Mutual dependence of the Arrhenius parameters results also from the change in the temperature interval of kinetic analysis. This is due to the poorly controlled reaction condition including the self-generated condition. In this respect, the CRTA has a merit, because the self-generated condition remains constant during the reaction, at least, compared with the traditional isothermal and non-isothermal measurements.

Therefore, the kinetic analysis of TA data cannot be successful unless the true value of the activation energy is known. The isoconversion method of calculating the activation energy is useful allowing to check the invariance of the activation energy during the course of reaction. For such TA curves providing the constant and characteristic value of E , the functional relationships $y(\alpha)$ and $z(\alpha)$ are very useful in elucidating the kinetic model function. These functions allow to check the applicability of the conventional physico-geometry based kinetic models and to extend the kinetic understanding based on the more sophisticated kinetic models.

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References

- 1) J. Sestak(ed.), Reaction Kinetics by Thermal Analysis, *Thermochim. Acta (Special issue)* **203**, 1992.
- 2) J. Sestak, *J. Therm. Anal.* **16**, 503 (1979); **33**,

- 1263 (1988).
- 3) J. Sestak, *Thermophysical Properties of Solids, Their Measurements and Theoretical Thermal Analysis*, Elsevier, Amsterdam (1984).
 - 4) J. Sestak, *J. Therm. Anal.* **36**, 1977 (1990).
 - 5) N. Koga, J. Sestak and J. Malek, *Thermochim. Acta* **188**, 333 (1991).
 - 6) J. Malek and J. M. Criado, *Thermochim. Acta* **203**, 25 (1992).
 - 7) J. Malek, *Thermochim. Acta* **200**, 257 (1992).
 - 8) E. S. Freeman and B. Carroll, *J. Phys. Chem.* **62**, 394 (1958).
 - 9) N. Koga and H. Tanaka, *J. Therm. Anal.*, in press.
 - 10) R. Ozao and M. Ochiai, *J. Ceram. Soc. Jpn.* **101**, 263 (1993).
 - 11) J. Sestak in D. Dollimore (ed.), *Thermal Analysis, Proc. 2nd ESTAC in Aberdeen*, J. Wiley, London (1981), p. 115.
 - 12) T. Kemeny and J. Sestak, *Thermochim. Acta* **110**, 113 (1987).
 - 13) J. Sestak and G. Berggern, *Thermochim. Acta* **3**, 1 (1971).
 - 14) V. M. Gorbachev, *J. Therm. Anal.* **18**, 194 (1980).
 - 15) N. Koga and J. Sestak, *Thermochim. Acta* **182**, 201 (1991).
 - 16) J. Sestak in H. G. Wiedeman (ed.), *Thermal Analysis, Proc. 6th ICTA*, Birkhauser, Stuttgart, Vol. 1 (1980), p. 29.
 - 17) J. Sestak, *J. Therm. Anal.* **33**, 1263 (1988).
 - 18) N. Koga and J. Sestak, *J. Therm. Anal.* **37**, 1103 (1991).
 - 19) N. Koga and H. Tanaka, *J. Therm. Anal.* **37**, 347 (1991).
 - 20) J. Flynn, *J. Therm. Anal.* **36**, 1269 (1990).
 - 21) J. Sestak, *Talanta* **13**, 567 (1966).
 - 22) H. Tanaka and N. Koga, *J. Therm. Anal.* **36**, 2601 (1990).
 - 23) N. Koga and H. Tanaka, *Thermochim. Acta* **183**, 125 (1991).
 - 24) J. Rouquerol, *J. Therm. Anal.* **5**, 203 (1973).
 - 25) H. Tanaka, *Netsu Sokutei* **19**, 32 (1992). (in Japanese)
 - 26) J. Malek, J. Sestak, F. Rouquerol, J. Rouquerol, J. M. Criado and A. Ortega, *J. Therm. Anal.* **38**, 71 (1992).
 - 27) J. P. Czarnecki, N. Koga, V. Sestakova and J. Sestak, *J. Therm. Anal.* **38**, 575 (1992).
 - 28) J. Sestak, *Phys. Chem. Glasses* **15**, 137 (1974).
 - 29) T. Ozawa, *Polymer* **12**, 150 (1971).
 - 30) T. Ozawa, *Bull. Chem. Soc. Jpn.* **57**, 639 (1984); 952 (1984).
 - 31) J. Sestak, *Thermochim. Acta* **98**, 339 (1986).
 - 32) N. Koga, J. Sestak and Z. Strnad, *Thermochim. Acta* **203**, 361 (1992).
 - 33) N. Koga and J. Sestak, *Bol. Soc. Esp. Ceram. Vidr.* **31**, 185 (1992).
 - 34) H. Tanaka and N. Koga, *J. Phys. Chem.* **92**, 7023 (1988).
 - 35) N. Koga and H. Tanaka, *J. Phys. Chem.* **93**, 7793 (1989).
 - 36) N. Koga and H. Tanaka, *Solid State Ion.* **44**, 1 (1990).
 - 37) T. Ozawa, *Thermochim. Acta* **203**, 159 (1992).
 - 38) T. Ozawa, *Bull. Chem. Soc. Jpn.* **38**, 1881 (1965).
 - 39) T. Ozawa, *J. Therm. Anal.* **2**, 301 (1970).
 - 40) H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).
 - 41) H. L. Friedman, *J. Polym. Sci., Part C* **6**, 183 (1964).
 - 42) T. Ozawa, *J. Therm. Anal.* **31**, 547 (1986).
 - 43) T. Ozawa, *Netsu Sokutei* **1**, 2 (1974). (in Japanese)
 - 44) T. Ozawa, *Thermochim. Acta* **100**, 109 (1986).
 - 45) N. Koga and H. Tanaka, *Thermochim. Acta*, in press.
 - 46) J. M. Criado, J. Malek and A. Ortega, *Thermochim. Acta* **147**, 377 (1989).
 - 47) J. Malek, *Thermochim. Acta* **138**, 337 (1989).
 - 48) J. Malek and J. M. Criado, *Thermochim. Acta* **164**, 199 (1990).
 - 49) J. Malek and V. Smrcka, *Thermochim. Acta* **186**, 153 (1991).
 - 50) J. Malek, *J. Non-Cryst. Solids* **107**, 323 (1989).
 - 51) V. M. Gorbachev, *J. Therm. Anal.* **27**, 151 (1983).
 - 52) P. D. Garn, *Thermochim. Acta* **135**, 71 (1988).

要 旨

非等温的速度論におけるデータ処理と

現象学的モデルの判別限界

固相反応の動力学的モデルは、厳密な等温的条件下での幾何学的に理想化された固体反応物に対する形式的な記述をもとにして導かれる。これらの仮定は、実際のプロセスに適合しない場合が多い。実際のプロセスと理想化された動力学的モデルとの差異は、得られる動力学的パラメータの真の値からの偏差としてあらわれる。この観点から、実際のプロセスをできるだけ正確に記述する経験的関数を用いることが有用である。この場合、不均一反応速度論のモデル関数は、より単純な均一反応速度論におけるモデル関数の歪曲したものであると考えられ、数学的には収容関数を掛け合わせるにより導く

ことができる。この経験的なモデル関数は、非等温的プロセスの等温的プロセスとの違いを収容するものとも考えられる。経験的に観察されるアレニウスパラメータの相互依存性は、熱分析における測定条件の制御に関する問題点と不適切な動力学的データ処理から生じることが多く、数学的にはアレニウスの関係式において速度定数が指数型で表されることと関係している。等変化率法では、ある反応のプロセス全体を通して活性化エネルギーが一定であることを確認することができ、以後の動力学的データ処理の指針となる。一定の活性化エネルギーが得られるプロセスに対しては、従来の速度式から導かれる二つの関数依存性を用いて動力学的モデル関数を決定することができる。