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NON-ISOTHERMAL KINETICS OF CONSECUTIVE REACTIONS

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Abstract

Theoretical consideration has been made of the non-isothermal kinetics of consecutive reactions based on the superposition principle. In the model the first reaction product reacts to form the final product and the two reactions proceed independently. The amount of the first reaction product and the production rate of the final product have been obtained as a function of time for isothermal cases and as a function of the reduced times for non-isothermal cases.

Keywords: consecutive reactions, EGA, evolved gas analysis, FTIR, non-isothermal kinetics, thermophotometry

Introduction

When thermoanalytical tools are limited to thermogravimetry, differential thermal analysis and differential scanning calorimetry, we can only observe changes of bulk physical properties, i.e., mass and enthalpy. With these tools, kinetic analysis can be precisely done only for a simple reaction, in which a single elementary process proceeds [1]. The one exception is the Avrami-Erofeev model for nucleation-and-growth processes in solid reactions and crystallizations. Their non-isothermal kinetics and a method to analyze such thermoanalytical data were published elsewhere [2, 3].

Nowadays, we have more powerful tools, such as thermophotometry with a Fourier transform IR spectrometer (FTIR) and evolved gas analysis (EGA) with a mass-spectrometer (MS) and/or an FTIR, by which we can observe chemical structural changes and/or we can determine volatilized products together with their volatilisation rates continuously. Therefore, we now have tools with which we can kinetically analyze other complex reactions consisting of multiple elementary processes, such as parallel competitive reactions and consecutive reactions. The present author and his co-worker published a method to kinetically analyze thermoanalytical data for parallel competitive reactions [4].

Consecutive reactions have been investigated for many years. For instance Braun and Rothman kinetically analyzed isothermal mass loss data of a consecutive

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reaction, i.e., pyrolysis of oil shale [5]. By introducing a thermal induction-time for the sample to heat up to the desired temperature, the data were well analyzed by a model of consecutive reactions, in which both the first and second reactions are first-order reactions. Similar studies on isothermal consecutive reactions are found in literature [6].

For non-isothermal kinetics of consecutive reactions, simulations have been mainly made and thermoanalytical curves have been calculated for specific cases to observe the effect of kinetic parameters on the calculated thermoanalytical curves [7–9]. Marcu and Segal [10] proposed a statistical method to analyze thermoanalytical data, in which kinetic parameters are estimated so as to minimize the difference between the data and the corresponding values calculated with the estimated parameters, and the best fitted estimation is obtained by iterative calculation. However, general and analytical equations for non-isothermal kinetics of consecutive reactions have not yet been proposed and they are necessary to prepare a method to analyze their data for future needs.

The author has made the first attempt to derive these equations for the non-isothermal kinetics of consecutive reactions by applying the superposition principle, and the results are presented in this paper. Controlled rate thermal analysis (CRTA) provides high resolution of reactions and some steps of consecutive reactions, such as multiple step dehydration, can be observed separately [10]. However, non-isothermal methods of obtaining the kinetics of consecutive reactions are still useful for thermoanalytical observation of consecutive reactions, because the temperature separation of some consecutive reactions might not be so large as to separately observe them, especially for cases where the second reaction proceeds faster than the first reaction. Non-isothermal methods are also useful for analysis in practical processes of these types of reactions.

Models

The types of reactions dealt with in this paper are as follows;

$$\mathrm{X}\rightarrow\mathrm{Y}+\mathrm{U}\uparrow \tag{1}$$

$$\mathrm{Y}\rightarrow\mathrm{Z}+\mathrm{V}\uparrow \tag{2}$$

where X, Y, U, Z and V are respectively, the original reactant, the non-volatile product of the first reaction, the volatile product of the first reaction, the non-volatile product of the second reaction and the volatile product of the second reaction. The first reaction and the following second reaction are independent of each other and the extent of reaction of one has no influence on the other.

The kinetic equation for the first reaction is:

$$\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}=k_1 f_1(\alpha_1) \tag{3}$$

and, when the second reaction proceeds without formation from X, the equation for the decreasing rate of Y by this reaction is:

$$\frac{\mathrm{d}\alpha_2}{\mathrm{d}t}=k_2 f_2(\alpha_2) \tag{4}$$

where

$$k_\mathrm{i}=A_\mathrm{i}\exp\left(-\frac{E_\mathrm{i}}{RT}\right) \tag{5}$$

and α, t, k, f, A, E, R and T are the extent of the reaction, the time, the rate constant, the function expressing the reaction mechanism, the pre-exponential factor, the activation energy, the gas constant and the absolute temperature, respectively, the subscripts indicating the reactions. The fractional amount of the reactant X is equal to $(1-\alpha_1)$.

Isothermal equations

First, let us consider the decrease in the amount of the product Y formed at a certain time, τ. The residual amount of this portion of Y at the time t, is expressed by $y(\tau,t)$. At a time τ,

$$y(\tau,\tau)=\left(\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}\right)_{t=\tau} \tag{6}$$

In Eq. (3) $\mathrm{d}\alpha_1/\mathrm{d}t$ is given as a function of α_1, but it can also be expressed as a function of time. Namely, if

$$\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}=k_1 f_1(\alpha_1) \tag{3}$$

then

$$\int\frac{\mathrm{d}\alpha_1}{f_1(\alpha_1)}=\int k_1\mathrm{d}t \tag{7}$$

and since the reaction proceeds isothermally, it is expressed for simplicity as follows:

$$F_1(\alpha_1)=k_1 t \tag{8}$$

where $F_1(\alpha_1)$ is equal to $\int\mathrm{d}\alpha_1/f_1(\alpha_1)$. Thus, α_1 can be expressed as a function of the time, and the derivative of α_1 can also be a function of k_1t so that we have the following equation and it is equal to $y(\tau,\tau)$

$$\left(\frac{\mathrm{d}\alpha_1}{\mathrm{d}t}\right)_{t=\tau}=f_1^{-1}(k_1\tau)=y(\tau,\tau) \tag{9}$$

where $f_1^{-1}(k_1t)$ is similar to the function of $f_1(\alpha_1)$ but $\mathrm{d}\alpha_1/\mathrm{d}t$ is given as a function of k_1t. $F(\alpha)$, $f(\alpha)$ and $f^{-1}(kt)$ are tabulated in Table 1.

Table 1 Forms of kinetic functions for different reaction mechanisms

Mechanism	$f(\alpha)=(\mathrm{d}\alpha/\mathrm{d}t)/k$	$F(\alpha)=\int \mathrm{d}\alpha/f(\alpha)$	$f^{-1}(kt)=(\mathrm{d}\alpha/\mathrm{d}t)^{*}$	$F^{-1}(kt)=\alpha^{*}$
n-th order ($n\neq1$)	$(1-\alpha)^{\mathrm{n}}$	$\{(1-\alpha)^{1-\mathrm{n}}-1\}/(n-1)$	$\{1+(n-1)kt\}^{\mathrm{n}/(1-\mathrm{n})}$	$1-\{1+(n-1)\mathrm{kt}\}^{1/(1-\mathrm{n})}$
1st order	$1-\alpha$	$-\ln(1-\alpha)$	$\exp(-kt)$	$1-\exp(-kt)$
Phase boundary-controlled contracting interface (cylinder)	$(1-\alpha)^{-1/2}/2$	$1-(1-\alpha)^{-1/2}$	$(1-kt)/2$	$1-(1-kt)^{-2}$
Phase boundary-controlled contracting interface (sphere)	$(1-\alpha)^{-2/3}/3$	$1-(1-\alpha)^{-1/3}$	$(1-kt)^{2}/3$	$1-(1-kt)^{-3}$

[*] The term *kt* in these equations can be replaced by $A\theta$

Next, we shall calculate $y(\tau,t)/y(\tau,\tau)$, the decreasing ratio of y at the time t to y at the time τ, and it can be derived by solving Eq. (4):

$$\int\frac{\mathrm{d}\alpha_2}{f_2(\alpha_2)}=\int k_2\mathrm{d}t \tag{10}$$

and this can be expressed for simplicity as follows:

$$F_2(\alpha_2)=\int k_2\mathrm{d}t \tag{11}$$

where $F_2(\alpha_2)$ is equal to $\int\mathrm{d}\alpha_2/f_2(\alpha_2)$. The range of this integration is from $t=\tau$ to the time $t=t$, and α_2 can be expressed as function of k_2t. Therefore:

$$\frac{y(\tau,t)}{y(\tau,\tau)}=F_2^{-1}(k_2t-k_2\tau) \tag{12}$$

where $F_2^{-1}(k_2t)$ is the inverse function of $F_2(\alpha_2)$ and $F_2^{-1}(k_2t)$ is equal to α_2. $F_2^{-1}(k_2t)$ is listed in Table 1. In Eq. (12), it is implicitly assumed that the decreasing amount of Y formed at one value of τ proceeds independently from Y formed at a different value of τ. Thus,

$$y(\tau,t)=f_1^{-1}(k_1\tau)F_2^{-1}(k_2t-k_2\tau) \tag{13}$$

Then we have the fraction of total Y at the time t, $\mathrm{Y}(t)$, as follows:

$$\mathrm{Y}(t)=\int_0^{t}y(\tau,t)\mathrm{d}\tau \tag{14}$$

and this logic is illustrated in Fig. 1. Thus, we have the general isothermal equation for consecutive reactions of the above model:

$$\mathrm{Y}(t)=\int_0^{t}f_1^{-1}(k_1\tau)F_2^{-1}(k_2t-k_2\tau)\mathrm{d}\tau \tag{15}$$

The rate of volatilisation of V may be derived. The decreasing rate of the product Y formed at τ is equal to the formation rate of V from the product Y formed at τ. If it is expressed as $\mathrm{v}'(\tau,t)$, then

$$\mathrm{v}'(\tau,t)=y(\tau,t)f_2^{-1}(k_2t-k_2\tau) \tag{16}$$

and

$$\left(\frac{\mathrm{dV}}{\mathrm{d}t}\right)_{t=t}=\int_0^{t}f_1^{-1}(k_1\tau)F_2^{-1}(k_2t-k_2\tau)f_2^{-1}(k_2t-k_2\tau)\mathrm{d}\tau \tag{17}$$

where $\mathrm{dV}/\mathrm{d}t$ is the fractional volatilisation rate of V. These equations [Eqs (15) and (17)] can be treated by Laplace transform.

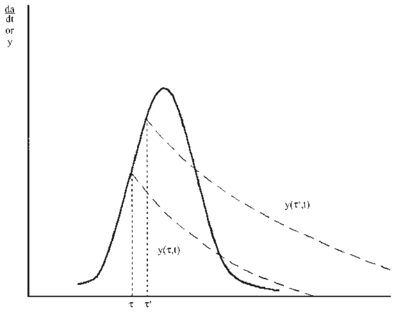

Fig. 1 Schematic drawing for change of reactants and products. The solid line is the curve for the production rate of Y (or the decreasing rate of X), and the broken lines are for *y*'s at different τ's. The amount of Y is the sum of the broken lines

General equations

The above Eqs (15) and (17) are the equations for isothermal consecutive reactions, and they can also be applied to non-isothermal cases, taking account of the temperature change and the temperature dependence of the rate constant. Therefore, kt in these equations should be replaced by $\int k\mathrm{d}t$ [Eqs (7), (8), (10) and (11)]. This can be done by introducing the reduced time, θ [1], because

$$\theta_i=\int\exp\left(-\frac{E_i}{RT}\right)\mathrm{d}t \tag{18}$$

and k_it or $\int k_i\mathrm{d}t$ can be replaced by $A_i\theta_i$. Furthermore,

$$\theta_2-\theta_2(\tau)=\int_0^t\exp\left(-\frac{E_1}{RT}\right)\mathrm{d}t-\int_0^\tau\exp\left(-\frac{E_1}{RT}\right)\mathrm{d}t \tag{19}$$

$$=\int_\tau^t\exp\left(-\frac{E_1}{RT}\right)\mathrm{d}t \tag{20}$$

Thus, we have

$$\mathrm{Y}(\theta_2)=\int_0^{\theta_2} f_1^{-1}[A_1\theta_1(\tau)]F_2^{-1}[A_2\theta_2-A_2\theta_2(\tau)]\exp\left(\frac{E_1}{RT}\right)\mathrm{d}\theta_2(\tau) \tag{21}$$

and

$$\left(\frac{\mathrm{dV}}{\mathrm{d}t}\right)_{\theta=\theta_2}= \tag{22}$$
$$=\int_0^{\theta_2} f_1^{-1}[A_1\theta_1(\tau)]F_2^{-1}[A_2\theta_2-A_2\theta_2(\tau)]f_2^{-1}[A_2\theta_2-A_2\theta_2(\tau)]\exp\left(\frac{E_1}{RT}\right)\mathrm{d}\theta_2(\tau)$$

where θ_1 and θ_2 are the reduced times for the first and second reactions, respectively, and $\theta_i(\tau)$ means that the reduced time is that at $t=\tau$.

Discussion

As seen in the above, the superposition principle is applied to derive Eqs (15), (17), (21) and (22), and this means that the decreasing rate of Y formed at τ is not influenced by Y formed at a different τ' and vice versa. In this principle, the rate of the first reaction is not influenced by the product of the second reaction and the rate constant of the second reaction is not influenced by the extent of the first reaction. These prerequisites are implicitly assumed in the above derivation.

A reaction consistent with these prerequisites is the case that the first reaction is every type of reaction except diffusion-controlled reactions and the second reaction is a first-order reaction. Diffusion-controlled reactions are excluded, because the diffusion constant must be changed by the second reaction. One boundary-controlled, contracting interface reaction followed by another are simple consecutive reactions for kinetics, but the logic is different from that in this paper.

Two reduced-times are involved in the non-isothermal equation, as seen in Eqs (21) and (22), so that the consecutive reactions under discussion are a system of multiple dimensions of time, and the relation between them is dependent on the temperature change. Therefore, we cannot calculate a priori these integrations as they are, but only for specific cases, such as constant rate heating.

When the sample is heated at a constant rate, we have the next relation, which may be useful in the calculation:

$$\frac{\theta_1}{\theta_2}=\frac{E_2}{E_1}\exp\left(\frac{E_2-E_1}{RT}\right) \tag{23}$$

because the reduced time can be approximated as follows [12]:

$$\theta_i=\frac{RT^2}{\beta E_i}\exp\left(-\frac{E_i}{RT}\right) \tag{24}$$

$$\frac{d\theta_1}{d\theta_2}=\exp\left(\frac{E_2-E_1}{RT}\right) \tag{25}$$

We can measure the volatilisation rates of U and V by EGA, for instance with MS and FTIR, and we can measure the amount of X, Y and Z in some cases by FTIR. These data can be combined to analyze the data and this may provide an easier way for analyzing the data.

The above consideration and the derived equations provide insight into the kinetics of the processes. For instance, when we observe the volatilisation rate of U, the kinetics becomes much simpler. The first reaction can be kinetically analyzed by using the volatilisation rate of U. Moreover, after the volatilisation rate of U becomes negligibly small, the decreasing rate of Y and the volatilisation rate of V follow their original kinetics [Eq. (4)], because the second reaction proceeds without the influence of the first reaction. Furthermore, the following can be deduced from Eqs (15), (17), (21) and (22). If we control the volatilisation rate of U at a fixed rate, as in CRTA, the value of the f_1^{-1} function is also controlled at the fixed value. Thus the decreasing rate of Y and the volatilisation rate of V follow relatively simple equations with one reduced time.

Other devices in experimental methods, such as the mode of the temperature change, and proper mathematical approximation should provide some methods for kinetic analysis in the future.

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