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Improved analytical model for isochronal transformation kinetics

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Abstract Analytical model for isochronal phase transformation kinetics attracts much attention for its advantages and importance. However, the simple but exact analytical formula of the isochronal transformation is unavailable because of the so-called temperature integral, and the asymptotic expansions have to be adopted to obtain approximate results. Here a generally used asymptotic expansion was proved divergent, and a reasonable approximation was proposed to obtain a more precise description as compared numerically to the previous one. Based on the proposed approximation, an analytical model for isochronal transformation kinetics was developed, which was proved more effective than the previous analytical model when the transformation occurs in a narrow temperature range and exhibited an identical form to the previous model when in a wide temperature interval.

Introduction

Phase transformation kinetics with its importance attains much attention both on experimental methods and theory analysis methods recently [1–3]. Based on the classical Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory [4–8], much progress has been made in the field of phase transformation kinetics [9–25]. For example, the JMAK model has been deeply modified to suit the isochronal cases [9–18], though its intention was aimed at the isothermal transformation. In [9], a path variable parameter depending on the thermal history was introduced so that the transformation fraction becomes a state function or functional of the path variable. A considerable improvement in analytical models of the isochronal kinetics has been made, especially in the area of so-called temperature integral [11–17]. The impingement modes are investigated in [18], while the nucleation modes are investigated in [19]. Monte Carlo method has also been adopted to simulate the phase transformation and the microstructural evolution in both isotropic and anisotropic cases [20–22], which deeply extended the validity and application of classical JMAK model. Furthermore, the combined JMAK models were adopted to investigate the overlapping transformation [23–25].

Compared with the isothermal transformation, the isochronal transformation and the associated isochronal kinetics attract more attention for their advantages in experimentation and industrial applications. The general isochronal kinetic analytical models are based on the transformation rate equation obtained from the isothermal transformation [10, 11] or the same impingement mode as isothermal transformation [12–17]. Generally, the so-called temperature integral is always encountered. However, an exact but simple expression is unavailable because of that temperature integral, and a number of recipes have been designed to cope with it. Even so, asymptotic expansions have to be adopted to get approximate results [10–17].

The model-analysis methods by fitting the experimental data with models provide an effective way to obtain the microstructure evolution kinetics from the bulk sample experiments [1–3]. Therefore, the effectiveness and validation of the model adopted become the key factors that affect the validity of the obtained kinetics results. Unexpectedly, the validity of a generally adopted asymptotic

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expansion was ignored, which will be shown here firstly. Another treatment for the temperature integral will be proposed on a strict mathematical basis to obtain a good approximation. Subsequently, an improved analytical model for isochronal transformation will be developed.

Theoretical background

The JMAK model

The JMAK model is often valid to describe the transformation kinetics involving nucleating randomly in the matrix and growing steadily until blocking by impinging [4–8, 12–17]. The transformation fraction (*f*) and the so-called extended transformation volume (V^e) can be calculated as:

$$f(t) = \frac{V^t(t)}{V} = 1 - \exp\left(-\frac{V^e(t)}{V}\right) \tag{1a}$$

$$V^e(t) = \int_0^t V\dot{N}[T(\tau)]Y(t,\tau)d\tau \tag{1b}$$

where T is the temperature, V is the matrix volume, $V^t(t)$ is the volume transformed, t and τ are the time, $\dot{N}$ is the nucleation rate, and Y is the volume of a single particle nucleated at τ.

For an isotropic case Y can be given as:

$$Y(t,\tau) = g\left[\int_\tau^t \upsilon[T(\gamma)]d\gamma\right]^{d/m} \tag{2}$$

where g is a geometrical factor, $\upsilon[T(t)]$ is the growth rate, d is the growth dimension ($d = 1, 2, 3$), and $m = 1, 2$ is the growth mode parameter. In the large undercooling or overheating case, the nucleation rate and growth rate can be generally given in Arrhenius form [15–17]:

$$\dot{N}[T(t)] = N_0 \exp\left(-\frac{Q_N}{RT(t)}\right) \tag{3}$$

$$\upsilon[T(t)] = \upsilon_0 \exp\left(-\frac{Q_G}{RT(t)}\right) \tag{4}$$

where Q_N and Q_G are the temperature-independent activation energy for nucleation and growth, respectively.

For an isothermal continuous nucleation and isotropic case, the classical JMAK model can be expressed as:

$$f = 1 - \exp(-K^n t^n) \tag{5}$$

where $K = k\exp\left(-\frac{Q}{RT}\right)$, $n = (d/m) + 1$, $k^n = \frac{gN_0\upsilon_0^{d/m}}{1+(d/m)}$, and $Q = \frac{Q_N + (d/m)Q_G}{n}$.

Subsequently, the transformation rate can be expressed as:

$$\frac{df}{dt} = nK(1-f)[-\ln(1-f)]^{(n-1)/n} \tag{6}$$

The general analytical model for isochronal transformation

A method called *isoconversion method* was often adopted to obtain the isochronal kinetics model, which was based on the transformation rate equation obtained from the isothermal transformation and the hypothesis that the isochronal transformation rate is dependent on temperature and the transformation fraction [10, 11]:

$$\frac{df}{dt} = F(f)K(T) \tag{7}$$

The expressions available for *F*(*f*) have been given in [26]. However, Eq. 6 was used mostly. Generally, the rate constant K is expected to be in a simple Arrhenius form with respect to temperature during the transformation [10, 11]:

$$K(T) = k\exp\left(-\frac{Q}{RT}\right) \tag{8}$$

Adopting the common expression (Eq. 6) for *F*(*f*) and integrating Eq. 7 with a linear heating rate:

$$\begin{aligned}
\int_0^f \frac{d\gamma}{F(\gamma)} &= \int_0^f \frac{d\gamma}{n(1-\gamma)[-\ln(1-\gamma)]^{(n-1)/n}} \\
&= \int_0^f \frac{d[-\ln(1-\gamma)]}{n[-\ln(1-\gamma)]^{(n-1)/n}} = [-\ln(1-f)]^{1/n} \\
&= \int_0^{t_f} K[T(t)]dt = \Phi^{-1}\int_{T_0}^{T_f} K(T)dT \\
&= \Phi^{-1}\int_{T_0}^{T_f} k\exp\left(-\frac{Q}{RT}\right)dT
\end{aligned} \tag{9}$$

Then,

$$f = 1 - \exp\left[-\left[\Phi^{-1}\int_{T_0}^{T_f} k\exp\left(-\frac{Q}{RT}\right)dT\right]^n\right] \tag{10}$$

where Φ is a temporally independent linear heating rate, and the integral $\int_{T_0}^{T_f} k\exp\left(-\frac{Q}{RT}\right)dT$ is the so-called temperature integral which is generally converted into another form [11, 15–17]:

$$\int_{T_0}^{T_f} k\exp\left(-\frac{Q}{RT}\right)dT = \frac{kQ}{R}\left[\int_{y_f}^{\infty}\frac{\exp(-\mathrm{y})}{y^2}dy - \int_{y_{\backslash 0}}^{\infty}\frac{\exp(-\mathrm{y})}{y^2}dy\right] = \frac{kQ}{R}[p(y_f)-p(y_0)] \tag{11a}$$

with

$$p(z) = \int_z^{\infty}\frac{\exp(-\mathrm{y})}{y^2}dy \tag{11b}$$

where $y = Q/RT$, $y_f = Q/RT_f$, $y_0 = Q/RT_0$, and the last term $p(y_0)$ in Eq. 11a is often ignored.

However, the Arrhenius behavior for rate constant K is not universal, but valid in the *isokinetic* case where the activation energies for nucleation and growth are equal or in the *site saturation* case where the nucleation is completed prior to crystal growth [17, 27–30]. For the more general cases, a reasonable treatment is incorporating the nucleation and growth modes into the isochronal kinetics and adopting the same impingement as isothermal transformation [12–17]. Then similar equation as Eq. 1 can be valid in isochronal transformation. Assuming both nucleation and growth are in Arrhenius forms as Eqs. 2–4, the extended volume (V^e) becomes:

$$V^e[T(t)] = \int_0^t V\dot{N}[T(\tau)]Y[(T(t),T(\tau)]d\tau = Vg\int_{T_0}^{T(t)} N_0\exp\left[-\frac{Q_\mathrm{N}}{RT(\tau)}\right]\left[\int_{T(\tau)}^{T(t)} \upsilon_0\exp\left(-\frac{Q_\mathrm{G}}{RT}\right)d\frac{T}{\Phi}\right]^{d/m} d\frac{T(\tau)}{\Phi} \tag{12}$$

It is shown that the temperature integral (Eq. 11a) still exists in Eq. 12. Therefore, one important procedure to attain the isochronal kinetics is treating the temperature integral exactly.

The temperature integral in the isochronal transformation kinetics

Validity of a previous asymptotic expansion

As the issue is limited in the temperature integral, the numerical method is valid to calculate the kinetics. However, the analytical model has drawn some attention for its advantage, especially when the kinetics needs determination from experiment by model analysis [1–3]. An exact but simple model is unavailable, and many recipes were designed to get approximate results [9–17]. Among those recipes, one of the most popular is the asymptotic expansion after a single integration-by-parts:

$$p(y) = \frac{\exp(-\mathrm{y})}{y^2}\left[1+\frac{2!}{-y}+\frac{3!}{(-y)^2}+\cdots+\frac{(n+1)!}{(-y)^n}+\cdots\right] \tag{13}$$

It can give reasonable precision for $p(y)$ by truncating the series at the first term in the common case: $15 < y < 60$ [10]. However, it will be shown later that the asymptotic expansion in Eq. 13 lacks a mathematical foundation. The series $a_i = \frac{(-1)^i(i+1)!}{y^i}$ in Eq. 13 where $i = 0, 1, 2, \ldots, \infty$, and their partial sums $A_i = \sum_{j=0}^{i}\frac{(-1)^j(j+1)!}{y^j}$ (its limitation is the part in square brackets of Eq. 13) are shown in Fig. 1a–c (where $y = 50$). In Fig. 1a ($i = 0\rightarrow 110$), the values of the series from the third term are almost zero, while their partial sum is almost 0.962. Seemingly, a possible good approximation for $p(y)$ can be obtained by truncating the series at the first term. However, the values of the series and their part sums are surging between -6×10^{19} and 2×10^{19} when $160 \leq i < 170$, e.g., $a_{160} = \frac{(-1)^{160}(160+1)!}{50^{160}} \approx 1.11 \times 10^{15}$ (see Fig. 1b). Their variation becomes more visible in a logarithm coordinate (see Fig. 1c). So, the validity of the asymptotic expansion in Eq. 13 has to be checked mathematically.

Considering the series $\sum_0^{\infty} a_i = \sum_0^{\infty}(-1)^i(i+1)!x^i = \sum_0^{\infty} b_i x^i$ $(i = 0, 1, 2, \ldots, \infty)$ in Eq. 13, where $b_i = (-1)^i(i+1)!$ are the coefficients of the series, and $x = y^{-1} = RT/Q$. The absolutely convergent radius of the series $\sum_0^{\infty} a_i$ (the Ratio Test) [31] is:

$$R = \lim_{i\to\infty}\frac{b_i}{b_{i+1}} = \lim_{i\to\infty}\left|\frac{(-1)^i(i+1)!}{(-1)^{i+1}(i+2)!}\right| = \lim_{i\to\infty}(i+2)^{-1} = 0 \tag{14}$$

which means that the absolutely convergent radius of x tends to zero or the series can only be absolutely convergent at $x = 0$ ($y = \infty$) [31]. Obviously, since y is finite as an actual parameter, the series $\sum_0^{\infty} a_i$ is impossible to be absolute convergent. After considering the alternation of the positives and the negatives, a new positive series can be obtained by combining the two neighbor terms:

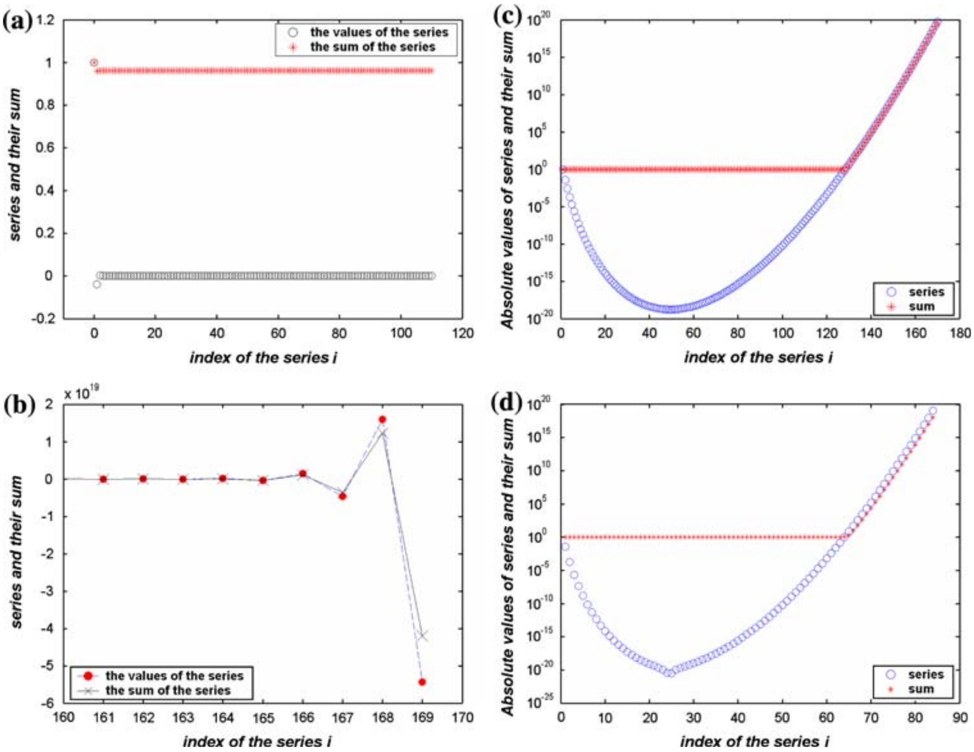


Fig. 1 The variation of the asymptotic expression of Eq. 13 (where $x = y^{-1} = RT/Q = 0.02$): (**a**) the first 110 terms of the series in Eq. 13 and their partial sum; (**b**) the terms between 160 and 169 of the series in Eq. 13 and their partial sum; (**c**) the first 170 terms in a logarithm coordinate of the series in Eq. 13 and their partial sum; (**d**) the series and their partial sum of Eq. 15 (which is deduced from Eq. 13)

$$\begin{aligned}\sum_1^\infty m_i &= \sum_1^\infty (a_{2i-1} + a_{2i})\\ &= \sum_1^\infty \left((-1)^{2i-1}(2i)!x^{2i-1} + (-1)^{2i}(2i+1)!x^{2i}\right)\\ &= \sum_1^\infty l_i x^{2i-1} \qquad (15)\end{aligned}$$

where $l_i = (2i + 1)!x–(2i)!$ (i is natural number) are the coefficients of the new series. The series in Eq. 15 with large index $\left(i > \frac{y-1}{2}\right)$ would have the positive sign, and then the series can be treated as a series with a positive sign. Subsequently, their absolute convergent radius is equal to their general convergent radius. It's obvious that if the series $\sum_0^\infty a_i$ is convergent, then the series $\sum_1^\infty m_i$ is convergent [31]. The series $\sum_1^\infty m_i$ and their partial sums are shown in Fig. 1d in a logarithm coordinate (where the absolute values for the primary terms with low index i are drawn), which shows the divergence of the new series. Similarly, the absolute convergent radius (also the general convergent radius) of the new series $\sum_1^\infty m_i$ (the Ratio Test) [31] is:

$$\begin{aligned}R &= \lim_{i\to\infty} \frac{l_i}{l_{i+1}} = \lim_{i\to\infty}\left|\frac{(2i+1)!x - (2i)!}{(2i+3)!x - (2i+2)!}\right|\\ &= \lim_{i\to\infty}\left|\frac{\frac{1}{2i+1} - x}{(2i+2) - (2i+2)(2i+3)x}\right|\\ &= \lim_{i\to\infty}\left|\frac{x}{(2i+2)(2i+3)x}\right| = \lim_{i\to\infty}\left|\frac{1}{(2i+2)(2i+3)}\right| = 0\end{aligned} \qquad (16)$$

where x is finite as an actual parameter. So, $\sum_1^\infty m_i$ can only be convergent at $x = 0$ ($y = \infty$). Consequently, $\sum_0^\infty a_i$ is impossible to be convergent. Therefore, the general asymptotic expansion in Eq. 13 for the temperature integral is unreasonable. However, it has been shown that the approximation from Eq. 13 by truncating the series at the first one or two terms promise a reasonable precision for $p(y)$ in the general case [10]. Actually, the asymptotic expansion for the temperature integral (Eq. 13) is obtained from single integration-by-parts [10], and its first step is:

$$\begin{aligned}p(y) &= \int_y^\infty \frac{\exp(-z)}{z^2}dz = -\frac{\exp(-z)}{z^2}\bigg|_y^\infty - 2\int_y^\infty \frac{\exp(-z)}{z^3}dz\\ &= \frac{\exp(-y)}{y^2} - 2\int_y^\infty \frac{\exp(-z)}{z^3}dz \qquad (17)\end{aligned}$$

Comparing the last integral with $p(y)$, for $y \le z < \infty$, then:

$$\begin{aligned}2\int_y^\infty \frac{\exp(-z)}{z^3}dz &< 2\int_y^\infty \frac{\exp(-z)}{yz^2}dz = \frac{2}{y}\int_y^\infty \frac{\exp(-z)}{z^2}dz\\ &= \frac{2}{y}p(y) \qquad (18)\end{aligned}$$

which means that the relative error would be less than $2/y$ for $p(y)$ by drawing the first term of Eq. 13. For the general case, $15 < y < 60$ [10], it does promise a reasonable precision for $p(y)$. It should be pointed out that it is not confused for the above seemingly inconsistent discussion, because the mistake in approximation for series in Eq. 13 has corrected the mistake in asymptotic expansion for Eq. 13.

An improved treatment for temperature integral

Because of its importance to obtain the isochronal transformation kinetics, precise treatment for temperature integral is expected. Here, the so-called temperature integral would be treated on an exact mathematical base:

$$\begin{aligned}
&\int_{T(\tau)}^{T(t)} \exp\left(-\frac{Q}{RT}\right)dT \\
&= \int_{T(\tau)}^{T(t)} \exp\left(-\frac{Q}{RT(t)}\right)\exp\left(\frac{Q}{RT(t)}-\frac{Q}{RT}\right)dT \\
&= \exp\left(-\frac{Q}{RT(t)}\right)\int_{T(\tau)}^{T(t)} \exp\left(\frac{Q}{RT(t)}-\frac{Q}{RT}\right)dT \\
&= \exp\left(-\frac{Q}{RT(t)}\right)\int_{T(\tau)}^{T(t)} \exp\left[\frac{Q[T-T(t)]}{RT\cdot T(t)}\right]dT
\end{aligned} \tag{19}$$

Similarly, an asymptotic expansion has been adopted to express the integrand in Eq. 19:

$$\begin{aligned}
&\exp\left[\frac{Q[T-T(t)]}{RT\cdot T(t)}\right] \\
&= \left\{\exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]\right\}^{\frac{T(t)}{T}} \\
&= \left\{\exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]\right\}^{1+\frac{T(t)-T}{T}} \\
&= \exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]\cdot\left\{\exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]\right\}^{\frac{T(t)-T}{T}} \\
&= \exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]\left\{1+(-1)\left[\frac{Q[T-T(t)]^2}{RT(t)^2T}\right]\right. \\
&\qquad \left.+\cdots+\frac{(-1)^i}{i!}\left[\frac{Q[T-T(t)]^2}{RT(t)^2T}\right]^i+\cdots\right\}
\end{aligned} \tag{20}$$

where the exponential series expansion has been adopted:

$$a^x = 1 + x\ln a + \cdots + \frac{(x\ln a)^i}{i!} + \cdots \quad \text{when } |x| < \infty \tag{21}$$

which is absolutely convergent. In Eqs. 20 and 21, $a = \exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]$, and $x = \frac{T(t)-T}{T}$.

Generally, $\frac{Q[T-T(t)]^2}{RT(t)^2T} \ll 1$, and as the positives and negatives alternate each other, a reasonable approximation can be available by adopting only the first term of the series in Eq. 20 to represent the series without bringing a significant error. Then temperature integral Eq. 19 can be calculated as:

$$\begin{aligned}
&\int_{T(\tau)}^{T(t)} \exp\left(-\frac{Q}{RT}\right)dT \\
&= \exp\left(-\frac{Q}{RT(t)}\right)\int_{T(\tau)}^{T(t)} \exp\left[\frac{Q[T-T(t)]}{RT\cdot T(t)}\right]dT \\
&\approx \exp\left(-\frac{Q}{RT(t)}\right)\int_{T(\tau)}^{T(t)} \exp\left[\frac{Q[T-T(t)]}{RT(t)^2}\right]dT \\
&= \exp\left(-\frac{Q}{RT(t)}\right)\frac{RT(t)^2}{Q}\left\{1-\exp\left[\frac{Q[T(\tau)-T(t)]}{RT(t)^2}\right]\right\}
\end{aligned} \tag{22}$$

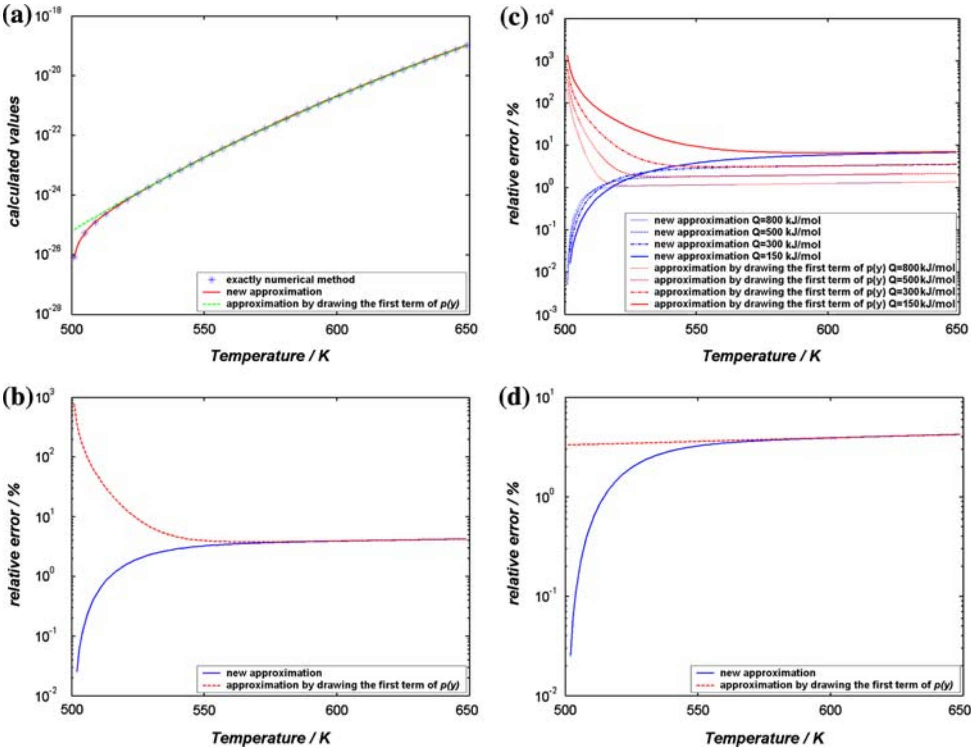
A comparison among the above approximation, the previous one by truncating the first term of $p(y)$ (Eq. 13) and the numerical calculation results of $\int_{T(\tau)}^{T(t)} \exp\left(-\frac{Q}{RT}\right)dT$, is conducted and shown in Fig. 2a–c, where the improved approximation varies tightly with the numerical result, while the previous approximation shows a reasonable precision at high temperature (or with a wide temperature interval) but deviates seriously at low temperature (or with a narrow temperature interval). It is also indicated by the relative errors (see Fig. 2b, c) that the approximation adopted here provides a better precision at lower temperature (or with a narrow temperature interval).

Furthermore, for wide temperature interval $T(\tau) - T(t) \ll 0$, then:

$$\begin{aligned}
&\exp\left(-\frac{Q}{RT(t)}\right)\frac{RT(t)^2}{Q}\left\{1-\exp\left[\frac{Q[T(\tau)-T(t)]}{RT(t)^2}\right]\right\} \\
&\approx \exp\left(-\frac{Q}{RT(t)}\right)\frac{RT(t)^2}{Q}
\end{aligned} \tag{23}$$

which means the previous approximation can be approached by the one proposed here with a large temperature interval. Even incorporating the term $p(y_0)$ generally ignored in Eq. 11a, the new approximation still promises a better precision (see Fig. 2d). Although the approximation by truncating the first term of $p(y)$ shows a reasonable precision

Fig. 2 A comparison of the approximation adopted here, the previous one by truncating the first term of $p(y)$ (Eq. 13) and the numerical calculation results of $\int_{T(\tau)}^{T(t)} \exp\left(-\frac{Q}{RT}\right)dT$ (**a**) results for $Q = 250$ kJ/mol, $T(\tau) = 500$ K, $T(t) = 650$ K, and T varies from 500 to 650 K; (**b**) the relative error in (**a**); (**c**) the relative error for $Q = 800$, 500, 300, and 150 kJ/mol; (**d**) the relative error calculated from the improved and the previous approximations comparing with the numerical calculation results, where the generally ignored term in Eq. 11a has been incorporated and $Q_G = 250$ kJ/mol, $T(\tau) = 500$ K, $T(t) = 650$ K, and T varies from 500 to 650 K



if introducing the generally ignored term $p(y_0)$ in Eq. 11a, it would be complex in the subsequent calculation of Eq. 12. Therefore, integrated merits of the proposed approximation here can be expected. It should be pointed out that the comparison conducted here is directed at the exact temperature integral Eq. 11a without dropping any term.

An improved analytical model for the isochronal kinetics

Expressions for transformed fraction

Based on the improved approximation for temperature integral and the general method for isochronal kinetics, an improved analytical model for isochronal transformation kinetics is available. The extended volume (Eq. 12) can be calculated as (see Appendix A):

$$V^{e}[T(t)] = \frac{VgN_0\upsilon_0^{d/m}}{Q_G^{d/m}} \exp\left(-\frac{Q_N + (d/m)Q_G}{RT(t)}\right) \left(\frac{RT(t)^2}{\Phi}\right)^{(d/m)+1} \psi(T_0, T(t), d/m)$$
$$= \frac{VK^n}{Q_G{}^{n-1}} \exp\left(-\frac{nQ}{RT(t)}\right) \left(\frac{RT(t)^2}{\Phi}\right)^{n} \psi(T_0, T(t), d/m) \qquad (24a)$$

where $K^n = gN_0\upsilon_0^{d/m}$, $n = (d/m) + 1$ and $Q = \frac{Q_N + (d/m)Q_G}{(d/m)+1}$. The expressions for $\psi(T_0, T(t), d/m)$ are listed in Table 1. Then, the transformation kinetics can be calculated by Eq. 1a:

$$f[T(t)] = 1 - \exp\left[-\frac{K^n}{Q_G{}^{n-1}} \exp\left(-\frac{nQ}{RT(t)}\right) \left(\frac{RT(t)^2}{\Phi}\right)^{n} \psi(T_0, T(t), d/m)\right] \qquad (24b)$$

Note that a term associated with the temperature T_0, the activation energy and the growth index is introduced in the improved analytical model as compared to that in [12–16]. If the transformation is conducted in a wide temperature interval, then $T_0 - T(t)$ is a large negative (heating process) with the transformation conducting so that $\exp\left(\frac{(Q_N + iQ_G)(T_0 - T(t))}{RT^2}\right)$ ($i = 0, 1, 2, \ldots$ see Table 1) can be ignored as compared with 1. Subsequently, $\psi(T_0, T(t), d/m)$ is almost a constant, e.g., for interface-controlled growth:

$$\psi(T_0, T(t), d/m) = \sum_{i=0}^{d/m} \binom{d/m}{i} \frac{(-1)^i}{Q_N + iQ_G} \left\{1 - \exp\left[\frac{(Q_N + iQ_G)[T_0 - T(t)]}{RT(t)^2}\right]\right\}$$
$$\approx \sum_{i=0}^{d/m} \binom{d/m}{i} \frac{(-1)^i}{Q_N + iQ_G} = \frac{(d/m)!\,Q_G^{d/m}}{\prod_{i=0}^{d/m} (Q_N + iQ_G)} \qquad (25)$$

Table 1 The expressions for ψ (T_0, $T(t)$, d/m)

Growth model	d/m	ψ (T_0, $T(t)$, d/m)
I-C[a]	1	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T)}{RT^2}\right)\right]-\frac{1}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T)}{RT^2}\right)\right]$
	2	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T)}{RT^2}\right)\right]-\frac{2}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T)}{RT^2}\right)\right]+\frac{1}{Q_N+2Q_G}\left[1-\exp\left(\frac{(Q_N+2Q_G)(T_0-T)}{RT^2}\right)\right]$
	3	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T)}{RT^2}\right)\right]-\frac{3}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T)}{RT^2}\right)\right]$ $+\frac{3}{Q_N+2Q_G}\left[1-\exp\left(\frac{(Q_N+2Q_G)(T_0-T)}{RT^2}\right)\right]-\frac{1}{Q_N+3Q_G}\left[1-\exp\left(\frac{(Q_N+3Q_G)(T_0-T)}{RT^2}\right)\right]$
D-C[b]	1/2	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T(t))}{RT(t)^2}\right)\right]-\frac{1/2}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T(t))}{RT(t)^2}\right)\right]-\frac{1/8}{Q_N+2Q_G}\left[1-\exp\left(\frac{(Q_N+2Q_G)(T_0-T(t))}{RT(t)^2}\right)\right]$
	1	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T)}{RT^2}\right)\right]-\frac{1}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T)}{RT^2}\right)\right]$
	3/2	$\frac{1}{Q_N}\left[1-\exp\left(\frac{Q_N(T_0-T(t))}{RT(t)^2}\right)\right]-\frac{3/2}{Q_N+Q_G}\left[1-\exp\left(\frac{(Q_N+Q_G)(T_0-T(t))}{RT(t)^2}\right)\right]$ $+\frac{3/8}{Q_N+2Q_G}\left[1-\exp\left(\frac{(Q_N+2Q_G)(T_0-T(t))}{RT(t)^2}\right)\right]+\frac{1/16}{Q_N+3Q_G}\left[1-\exp\left(\frac{(Q_N+3Q_G)(T_0-T(t))}{RT(t)^2}\right)\right]$

[a] I-C = Interface-controlled growth

[b] D-C = Diffusion-controlled growth

Then, the extended volume V^e becomes:

$$V^e[T(t)] \approx \frac{VgN_0\upsilon_0^{d/m}}{{Q_G}^{d/m}}\sum_{i=0}^{d/m}\binom{d/m}{i}\frac{(-1)^i}{Q_N+iQ_G}\exp\left(-\frac{Q_N+(d/m)Q_G}{RT(t)}\right)\left(\frac{RT(t)^2}{\Phi}\right)^{(d/m)+1}$$
$$=\frac{VgN_0\upsilon_0^{d/m}(d/m)!}{\prod_{i=0}^{d/m}(Q_N+iQ_G)}\exp\left(-\frac{Q_N+(d/m)Q_G}{RT(t)}\right)\left(\frac{RT(t)^2}{\Phi}\right)^{(d/m)+1} \tag{26}$$

which is identical to the model in [12–17] (if $p(y)$ adopting the first term of Eq. 13 in [17]). However, the term $\exp\left(\frac{(Q_N+iQ_G)(T_0-T(t))}{RT^2}\right)$ in $\psi(T_0,\ T(t),\ d/m)$ is comparable with 1 for a narrow temperature interval, thereby bringing larger error if this term is ignored in $\psi(T_0,\ T(t),\ d/m)$. Hence, the analytical model proposed here would bring a better description, especially for the transformation completed in a narrow temperature interval.

Expressions for transformation rate

For some of the transformation kinetic experimental data obtained, such as DSC curves, the experimental data actually represent the transformation rate [1–3]. If differentiating the transformed fraction formula directly, the formula Eq. 24b would give a complex form. Thus, a simple or maybe more precise formula in transformation rate is required.

From the transformation fraction: $f[T(t)] = 1 - \exp\left(-\frac{V^e[T(t)]}{V}\right)$, the transformation rate can be calculated as: $\alpha[T(t)] = \frac{df[T(t)]}{dT(t)} = \exp\left(-\frac{V^e[T(t)]}{V}\right)\frac{dV^e[T(t)]}{VdT(t)}$ (in linear heating isochronal transformation). Then, the issue is limited into calculating the differential of the extend volume V^e given in Eq. 12. Then:

$$\frac{dV^e_{d/m}[T(t)]}{dT(t)}$$
$$=\frac{d\left[V\int_{T_0}^{T(t)}N_0\exp\left(-\frac{Q_N}{RT(\tau)}\right)g\left[\int_{T(\tau)}^{T(t)}\upsilon_0\exp\left(-\frac{Q_G}{RT}\right)d\frac{T}{\Phi}\right]^{d/m}d\frac{T(\tau)}{\Phi}\right]}{dT(t)}$$
$$=\frac{d}{m}\upsilon_0\Phi^{-1}\exp\left(-\frac{Q_G}{RT(t)}\right)\left[V\int_{T_0}^{T(t)}N_0\exp\left(-\frac{Q_N}{RT(\tau)}\right)g\left[\int_{T(\tau)}^{T(t)}\upsilon_0\exp\left(-\frac{Q_G}{RT}\right)d\frac{T}{\Phi}\right]^{(d/m)-1}d\frac{T(\tau)}{\Phi}\right]$$
$$=\frac{d}{m}\upsilon_0\Phi^{-1}\exp\left(-\frac{Q_G}{RT(t)}\right)V^e_{(d/m)-1}[T(t)]$$
$$\approx\frac{d}{m}\frac{VgN_0\upsilon_0^{d/m}}{\Phi Q_G^{(d/m)-1}}\exp\left(-\frac{Q_N+(d/m)Q_G}{RT(t)}\right)\left(\frac{RT(t)^2}{\Phi}\right)^{d/m}\psi(T_0,T(t),(d/m)-1) \tag{27}$$

where Eq. 24a and the relation:

$$V[T(t)] = \int_{T_0}^{T(t)} \varphi[T(\tau), T(t)] dT(\tau) \tag{28a}$$

and

$$\frac{dV[T(t)]}{dT(t)} = \varphi[T(\tau), T(t)] + \int_{T_0}^{T(t)} \frac{\partial \varphi[T(\tau), T(t)]}{\partial T(t)} dT(\tau) \tag{28b}$$

have been used. Here,

$$\begin{aligned} &\varphi[T(\tau), T(t)] \\ &\quad = N_0 \exp\left(-\frac{Q_\mathrm{N}}{RT(\tau)}\right) g \left[\int_{T(\tau)}^{T(t)} \upsilon_0 \exp\left(-\frac{Q_\mathrm{G}}{RT}\right) d\frac{T}{\Phi}\right]^{d/m} \end{aligned} \tag{28c}$$

Since the procedure of approximation after differentiation may produce less deviation than that before differentiation, a probably more precise transformation rate formula can be given as:

$$\begin{aligned} \alpha[T(t)] = &\exp\left(-\frac{V^\mathrm{e}_{d/m}[T(t)]}{V}\right) \frac{d}{m} \upsilon_0 \Phi^{-1} \\ &\exp\left(-\frac{Q_\mathrm{G}}{RT(t)}\right) \frac{V^\mathrm{e}_{(d/m)-1}[T(t)]}{V} \\ &\approx \frac{d}{m} \Phi^{-1} \exp\left[-\frac{K^n}{{Q_\mathrm{G}}^{n-1}} \exp\left(-\frac{nQ}{RT(t)}\right)\right. \\ &\left.\left(\frac{RT(t)^2}{\Phi}\right)^n \psi(T_0, T(t), d/m)\right] \\ &\times \frac{K^n}{{Q_\mathrm{G}}^{n-2}} \exp\left(-\frac{nQ}{RT(t)}\right) \left(\frac{RT(t)^2}{\Phi}\right)^{n-1} \\ &\psi(T_0, T(t), (d/m) - 1) \end{aligned} \tag{29}$$

A comparison of the improved analytical model (Eq. 29) and the previous one (based on Eq. 26) has been conducted and presented in Fig. 3. It is found that the improved analytical model varies tightly with the data of numerical method in a wide range of applied heating rates, while the previous model promises a reasonable precision at high heating rate (or with a wide transformation temperature interval). So, the improved analytical model would provide better description for a transformation completed in a narrow temperature interval.

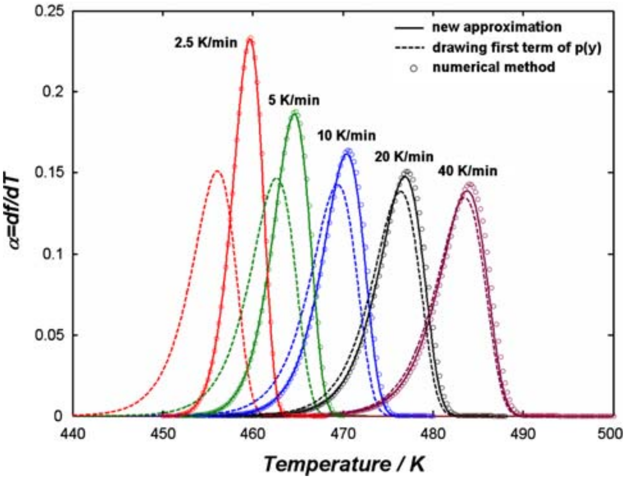


Fig. 3 A comparison of the adopted approximation in Eq. 29 (*solid curves*), the previous approximation based on Eq. 26 (*dashed curves*) and the numerical calculation results (*circles*) by adopting $Q_\mathrm{N} = 230$ kJ/mol, $Q_\mathrm{G} = 160$ kJ/mol, $K = 1.414 \times 10^{18}\ \mathrm{s}^{-1}$, $d/m = 3$, $T_0 = 450$ K under the applied heating rates of 40, 20, 10, 5, and 2.5 K/min

Though various approximations for the temperature integral can be available in the literatures [10–16], the approximations proposed here are more suitable for the general cases where nucleation modes and growth mechanism are incorporated into isochronal transformation kinetics, while the other approximations for the temperature integral are limited in the *isoconversion* method. It is because the calculation of double temperature integral in Eq. 12 requires further simplification after the first step of temperature integral. The approximation in [17] which is based on Eq. 13 may promise a better precision if not adopting the first term approximation for $p(y)$ in Eq. 13 but the first two or more terms (not the more the better). There, a further attempt is needed for the diffusion-controlled growth case in [17]. Therefore, the analytical model developed here can be expected to have a good performance in some transformations completed in a narrow temperature interval.

Conclusions

This work focuses on the analytical model of isochronal transformation kinetics. The following conclusions can be drawn:

(i) One of the most widely used asymptotic expansions for the so-called temperature integral is proved to be divergent.

(ii) A reasonable treatment for the temperature integral has been proposed by adopting an absolute convergent series. Upon that, an analytical model for isochronal transformation kinetics has been developed, which is identical to the previous model when the transformation is completed in a wide temperature interval while differs distinctly when the transformation is completed in a narrow temperature interval.

(iii) The proposed treatment for the temperature integral and the consequent analytical model for isochronal transformation kinetics have been proved more effective than the previous ones, especially in a narrow temperature interval by numerical method.

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Appendix A: Deducing the expression for the isochronal transformation kinetics model

The extend volume Eq. 12 can be calculated upon Eq. 22:

$$\begin{aligned} V^{e}[T(t)] &= \frac{VgN_0\upsilon_0^{d/m}}{\Phi^{(d/m)+1}}\exp\left(-\frac{(d/m)Q_{\mathrm{G}}}{RT(t)}\right)\left(\frac{RT(t)^2}{Q_{\mathrm{G}}}\right)^{d/m} \\ &\quad \cdot\int_{T_0}^{T(t)}\exp\left(-\frac{Q_{\mathrm{N}}}{RT(t)}\right) \\ &\quad \left\{1-\exp\left[\frac{Q_{\mathrm{G}}[T(\tau)-T(t)]}{RT(t)^2}\right]\right\}^{d/m} dT(\tau) \\ &= \frac{VgN_0\upsilon_0^{d/m}}{\Phi^{(d/m)+1}}\exp\left(-\frac{Q_{\mathrm{N}}+(d/m)Q_{\mathrm{G}}}{RT(t)}\right) \\ &\quad \left(\frac{RT(t)^2}{Q_{\mathrm{G}}}\right)^{d/m}\cdot\int_{T_0}^{T(t)}\exp\left[\frac{Q_{\mathrm{N}}[T(\tau)-T(t)]}{RT(t)^2}\right] \\ &\quad \left\{1-\exp\left[\frac{Q_{\mathrm{G}}[T(\tau)-T(t)]}{RT(t)^2}\right]\right\}^{d/m} dT(\tau) \end{aligned} \tag{A1}$$

The power term in (A1) can be expanded as binomial series [14, 31]:

$$\begin{aligned} &\left\{1-\exp\left[\frac{Q_{\mathrm{G}}[T(\tau)-T(t)]}{RT(t)^2}\right]\right\}^{d/m} \\ &\quad = \sum_{i=0}^{\infty}\binom{d/m}{i}(-1)^i\exp\left[\frac{iQ_{\mathrm{G}}[T(\tau)-T(t)]}{RT(t)^2}\right] \end{aligned} \tag{A2}$$

where $\binom{d/m}{i} = \frac{\prod_{j=0}^{i-1}((d/m)-j)}{i!}$, $\binom{d/m}{0} = 1$, is the binomial coefficients. Then the integral (A1) can be calculated as:

$$\begin{aligned} V^{e}[T(t)] &= \frac{VgN_0\upsilon_0^{d/m}}{\Phi^{(d/m)+1}}\exp\left(-\frac{Q_{\mathrm{N}}+(d/m)Q_{\mathrm{G}}}{RT(t)}\right)\left(\frac{RT(t)^2}{Q_{\mathrm{G}}}\right)^{d/m} \\ &\quad \times\int_{T_0}^{T(t)}\exp\left[\frac{Q_{\mathrm{N}}[T(\tau)-T(t)]}{RT(t)^2}\right]\sum_{i=0}^{\infty}\binom{d/m}{i}(-1)^i \\ &\quad \exp\left[\frac{iQ_{\mathrm{G}}[T(\tau)-T(t)]}{RT(t)^2}\right]dT(\tau) \\ &= \frac{VgN_0\upsilon_0^{d/m}}{\Phi^{(d/m)+1}}\exp\left(-\frac{Q_{\mathrm{N}}+(d/m)Q_{\mathrm{G}}}{RT(t)}\right)\left(\frac{RT(t)^2}{Q_{\mathrm{G}}}\right)^{d/m} \\ &\quad \sum_{i=0}^{\infty}\binom{d/m}{i}(-1)^i \\ &\quad \int_{T_0}^{T(t)}\exp\left[\frac{(Q_{\mathrm{N}}+iQ_{\mathrm{G}})[T(\tau)-T(t)]}{RT(t)^2}\right]dT(\tau) \\ &= \frac{VgN_0Q_{\mathrm{G}}\upsilon_0^{d/m}}{\Phi^{(d/m)+1}}\exp\left(-\frac{Q_{\mathrm{N}}+(d/m)Q_{\mathrm{G}}}{RT(t)}\right) \\ &\quad \left(\frac{RT(t)^2}{Q_{\mathrm{G}}}\right)^{(d/m)+1}\sum_{i=0}^{\infty}\binom{d/m}{i}\frac{(-1)^i}{Q_{\mathrm{N}}+iQ_{\mathrm{G}}} \\ &\quad \left\{1-\exp\left[\frac{(Q_{\mathrm{N}}+iQ_{\mathrm{G}})[T_0-T(t)]}{RT(t)^2}\right]\right\} \\ &= \frac{VgN_0\upsilon_0^{d/m}}{Q_{\mathrm{G}}{}^{d/m}}\exp\left(-\frac{Q_{\mathrm{N}}+(d/m)Q_{\mathrm{G}}}{RT(t)}\right) \\ &\quad \left(\frac{RT(t)^2}{\Phi}\right)^{(d/m)+1}\psi(T_0,T(t),d/m) \end{aligned} \tag{A3}$$

where

$$\begin{aligned} \psi(T_0,T(t),d/m) &= \sum_{i=0}^{\infty}\binom{d/m}{i}\frac{(-1)^i}{Q_{\mathrm{N}}+iQ_{\mathrm{G}}} \\ &\quad \left\{1-\exp\left[\frac{(Q_{\mathrm{N}}+iQ_{\mathrm{G}})[T_0-T(t)]}{RT(t)^2}\right]\right\} \end{aligned} \tag{A4}$$

For the interface-controlled growth, *d*/*m* is integer, the binomial coefficients would be truncated at $i = d/m$, and then (A2) becomes:

$$\begin{aligned} \psi(T_0,T(t),d/m) &= \sum_{i=0}^{d/m}\binom{d/m}{i}\frac{(-1)^i}{Q_{\mathrm{N}}+iQ_{\mathrm{G}}} \\ &\quad \left\{1-\exp\left[\frac{(Q_{\mathrm{N}}+iQ_{\mathrm{G}})[T_0-T(t)]}{RT(t)^2}\right]\right\} \end{aligned} \tag{A5}$$

For the diffusion-controlled growth, *d*/*m* is semi-integer except $d/m = 2/2$, and then $\psi(T_0, T(t), d/m)$ has infinite terms. However, $\psi(T_0, T(t), d/m)$ converges quickly [14]. Therefore, a reasonable approximation can be available by truncating at the primary terms. The expressions for $\psi(T_0, T(t), d/m)$ are given in Table 1.

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