MELTING OF GLASS BATCH: MODEL FOR MULTIPLE OVERLAPPING GAS-EVOLVING REACTIONS

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Abstract
In this study, we present a model for the kinetics of multiple overlapping reactions. Mathematical representation of the kinetics of gas-evolving reactions is crucial for the modeling of the feed-to-glass conversion in a waste-glass melter. The model simulates multiple gas-evolving reactions that occur during heating of a high-alumina high-level waste melter feed. To obtain satisfactory kinetic parameters, we employed Kissinger’s method combined with least-squares analysis. The power-law kinetics with variable reaction order sufficed for obtaining excellent agreement with measured thermogravimetric analysis data.

Keywords: overlapping reactions, reaction kinetics, Kissinger method, glass melting, glass batch, TGA

Introduction
Successive and simultaneous reactions are common in reacting mixtures, and multiple overlapping reactions are typical in glass batches during their conversion to molten glass [1-
Yet hardly any mixture found in nature or industrial technology has as many components and undergoes as many reactions as melter feeds during vitrification of nuclear wastes [20, 21]. The waste itself contains compounds of 40 to 60 elements [22] that react with glass-forming additives on heating. Consequently, the non-isothermal thermogravimetric analysis (TGA) of high-level waste melter feeds reveals multiple overlapping peaks on the $d\xi/dt$ versus $T$ curve, where $\xi$ is the conversion progress, $t$ is the time, and $T$ is the temperature. These reactions occur within the cold cap, a layer of melter feed floating on the pool of molten glass in the melter [23, 24]. The feed is charged on the top of the cold cap, where the temperature is $\sim 100^\circ$C, and as it moves towards the bottom, where the temperature is $\sim 1000^\circ$C, it is converted to glass [25, 26]. A model for the conversion kinetics is needed for the cold cap model that in turn is a part of the model of the melter.

In this paper, we analyze the gas evolution process as recorded by the non-isothermal TGA. We do not attempt to assess the mechanisms of individual gas-evolving reactions from solid and liquid components, which are both successive and simultaneous and include the release of chemically bonded water, reactions of nitrates with organics, and reactions of molten salts with solid silica. We merely assume that the reactions are independent and their rates can be described by the equation $-d\xi/dt = f_i(\xi_i)A_i\exp(-B_i/T)$, where $f_i(\xi_i) = \xi_i^{n_i}$ is a power-law function, $\xi$ is the degree of conversion, $A$ is the pre-exponential factor, $B$ is the activation energy, $n$ is the (apparent) reaction order, and the subscript $i$ stands for the $i$th reaction. Our goal is to model the reaction kinetics in a way that is sufficient and adequate for modeling of the cold cap process. To this end, we deem the four-parameter simulation for each reaction satisfactory. These parameters are $A_i$, $B_i$, $n_i$, and $w_i$, the weight of the $i$th reaction (the fraction of the total mass loss caused by the $i$th reaction). Considering the number of reactions, this number of parameters is too large to effectively optimize with least-squares
regression, especially for less distinct peaks. Therefore, we applied Kissinger’s method [27] for the direct estimate of $B_i$s based on the shift of the peak maximum temperature with the rate of heating and used least-squares optimization for the remaining parameters. The kinetics of reactions with overlapping peaks has been investigated since 1980s [28–36] and the two-step optimization was employed by several researchers [30, 31, 32, 36].

**Theory**

The mechanisms of reactions that occur during the conversion of melter feeds to glass are complex. Fortunately, the power-law function satisfactorily describes most of the gas-evolving melting reactions monitored by the TGA, allowing us to choose the standard power-law kinetics, according to which the rate of gas-evolving reactions can be expressed as

$$\frac{dx_i}{dt} = A_i (1 - x_i)^n \exp\left(-\frac{B_i}{T}\right)$$

where $x_i$ is the fraction of material reacted in the $i$th reaction.

In his seminal paper, Kissinger [27] derived for $B_i$ the formula

$$B_i = -\frac{d\left(\ln\frac{\Phi}{T_{im}^2}\right)}{d\left(\frac{1}{T_{im}}\right)}$$

where $\Phi = dT/dt$ is the temperature increase rate and the subscript $m$ denotes the peak maximum $(d^2x_i/dt^2 = 0)$. This approximate formula is highly applicable for batch melting reactions, as shown in Appendix A.
If $\Phi$ is constant and $n \neq 1$, integration of Eq. (1) yields

$$
 x_i = 1 - \left[ 1 + \frac{(n_i - 1)A_i}{\Phi} \int_0^T \exp \left( -\frac{B_i}{T} \right) dT \right]^{1/(1-n_i)}
$$

(3)

Following Kissinger, who used Murray and White’s approximation for the exponential integral [37], Eq. (3) becomes

$$
 x_i = 1 - \left[ 1 + \frac{(n_i - 1)A_i T^2}{B_i \Phi} \left( 1 - \frac{2T}{B_i} \right) \exp \left( -\frac{B_i}{T} \right) \right]^{1/(1-n_i)}
$$

(4)

This expression allows us to eliminate $x$ from Eq. (1), thus expressing $dx_i/dT$ as a function of $T$ and $\Phi$ alone.

For multiple reactions that are mutually independent, we can write (using $T = T_0 + \Phi t$)

$$
 \frac{dx}{dT} = \frac{1}{\Phi} \sum_i w_i A_i (1 - x_i)^{n_i} \exp \left( -\frac{B_i}{T} \right)
$$

(5)

where $x = \Sigma x_i$.

Experimental

Table 1 displays the composition of the melter feed used. As described elsewhere [21], this feed was formulated to vitrify a high-alumina high-level waste to produce glass of the composition (with mass fractions in parentheses): SiO$_2$ (0.305), Al$_2$O$_3$ (0.240), B$_2$O$_3$ (0.152), Na$_2$O (0.096), CaO (0.061), Fe$_2$O$_3$ (0.059), Li$_2$O (0.036), Bi$_2$O$_3$ (0.011), P$_2$O$_5$ (0.011), F
(0.007), \(\text{Cr}_2\text{O}_3\) (0.005), \(\text{PbO}\) (0.004), \(\text{NiO}\) (0.004), \(\text{ZrO}_2\) (0.004), \(\text{SO}_3\) (0.002), \(\text{K}_2\text{O}\) (0.001), \(\text{MgO}\) (0.001), and \(\text{ZnO}\) (0.001). This glass was designed for the Hanford Tank Waste Treatment and Immobilization Plant, currently under construction at the Hanford Site in Washington State, USA.

The simulated melter feed was prepared, as described by Schweiger et al. [21], as slurry that was dried at 105°C overnight in an oven. For the TGA, feed samples of 10–60 mg were placed in a Pt crucible from TA Instruments® (New Castle, DE, U.S.A., SDT-Q600) and heated from ambient temperature (≈25°C) to 1200°C at the rates 1, 5, 10, 15, 20, and 50 K/min.

Fig. 1 shows the TGA curves for the melter feed heated at several rates. As expected, the peaks shift to higher temperatures and the peak heights generally decrease as the rate of heating increases.

To deconvolute the TGA curve of \(\frac{dx}{dT}\) versus \(T\) for a series of \(\Phi_s\), \(T_{ms}\) were determined as temperatures of the peak maxima or estimated for shoulders on larger peaks. From these data, with Eq. (2), we obtained \(B_s\). Having predetermined \(B_s\) facilitated the application of the least squares analysis that we employed to fit the combined Eqs. (4) and (5) to measured \(\frac{dx}{dT}\) versus \(T\) data to obtain three independent parameters, \(A_i\), \(n_i\), and \(w_i\), for each reaction.

**Results**

In our previous work [23], we fitted Eq. (5) with \(n_i = 1\) to experimental data, taking advantage of the fact that with \(n_i = 1\) one can calculate \(A_i\) using the formula \(A_i = (B_i\Phi/T_{mi})^{2}\exp(B/T_{mi})\). Fig. 2 displays the results of the least-squares analysis for eight major reactions. Clearly, the agreement of measured and calculated curves is far from satisfactory: 1) the conversion rates are underestimated between peaks 1 and 2 and peaks 4 and 5; 2) the
long tail of peak 8 is not well simulated; 3) some calculated peaks overshoot the measured
peaks.

To improve the model, we upgraded it to the $n^{th}$-order reaction model and added reaction
1A between reactions 1 and 2. For the overlapped reactions, such as 1A, we obtained the $T_m$
by subtracting the neighboring peaks as calculated from the measured curve. Figure 3 displays
the Kissinger plot for all nine peaks. Table 2 lists the values of $B$ calculated with Eq. (2),
together with the standard deviations and the coefficients of determination, $R^2$. Table 3 lists
the result of the least-squares analysis and Fig. 4 displays the deconvoluted TGA curve for the
heating rate 15 K/min.

As Fig. 4 shows, peak 8 possesses a long tail, which is probably caused by a process with
a temperature-dependent $B_8$ or by a conglomerate of multiple reactions. The algorithm for the
least-squares analysis simulates this long tail via a high value of the reaction order. The fitted
$n_i$s were also abnormally high for some other peaks (peak 5, as can be seen in Table 3, and
peaks 1, 1A, and 7 in similar fits to some other heating rates). Because these elongated peaks
unduly influence the neighboring peaks, we constrained $n_i$s for peaks 1, 1A, 5, and 7 to $0 < n_i$
< 2 but we left peak 8 to retain an unrestricted reaction order to represent the evolution of gas
at high temperatures as faithfully as possible. Peak 8 gases might be responsible for foaming
that affects, and perhaps even controls, the melting rate of the cold cap in the waste glass
melter [23, 25]. Tables 4, 5 and 6 present the values of the kinetic coefficients $A_i$ and $n_i$ and
the reaction weights, $w_i$, from fitting joined Eqs. (4) and (5) to the TGA curves.

Assuming that the kinetics of individual reactions does not change with the heating rate
(Kissinger’s formula is based on this assumption), the parameters $A_i$ and $n_i$ are independent of
$\Phi$. Indeed, as the very small values of standard deviation in Table 4 indicate, $\log(A_i)$ values
are almost constant and their averages represent the averaged pre-exponential factors for
individual reactions across the heating rates employed.
Somewhat larger standard deviations of \( n_i \)s (up to 39%) indicate differences in the shapes of the peaks, but no trends can be discerned from the values. The \( n_i \) values of peaks with negligible weights (those in parentheses) were not included in the averages listed in Table 5 (see the virtually nonexistent peak 5 in Figs. 4 and 5). Note that \( n_i = 2 \) was imposed as the upper limit for peaks 1, 1A, 5 and 7.

On the other hand, \( w_i \) can vary with \( \Phi \), as consecutive reactions may be influenced by preceding ones, i.e., reactions that run at a lower temperature affect the reactions that follow them, especially when the heating rate is low. Accordingly, some reactions are not independent, but not to the extent that would invalidate the superposition relationship, Eq. (5).

Table 7 lists \( w_i \) values recalculated using the average values of \( A_i \) and \( n_i \) listed in Tables 4 and 5. Since \( w_i \) is the fraction of the material reacted by \( i^{th} \) reaction, the sum of the \( w_i \)'s for all reactions, \( w = 0.202 \pm 0.003 \), represents the total mass loss during the heat treatment. Table 7 also lists the measured values of fractional mass loss, \( w_{TGA} \). Fig. 6 plots the corresponding comparisons of measured and calculated TGA curves together with the peak deconvolution.

Discussion

Our present objective is describing the gas evolution from a melter feed in a way suitable for implementing its kinetics into a mathematical model of the cold cap response to the conditions in the glass melter. To this end, Eq. (5) with the numerical values of parameters is adequate even though the \( f_i(x_i) = (1 - x_i)^n \) used does not represent the reaction mechanism. Provided that the values of \( A_i \) and \( n_i \) are independent of \( \Phi \), the only task left is to construct reasonable functions of \( w_i \)'s versus \( \Phi \), at least for the rates within the interval of 5 to 20 K/min that exist within the cold cap. As evidenced from Table 7, the \( w_i \) versus \( \Phi \) values significantly deviate from constancy, at least for some peaks. Only \( w_1 \) is virtually independent of \( \Phi \). While some \( w_i \)'s fluctuate because of experimental error, some peaks exhibit discernible trends for
which an approximation function $w_i(\Phi)$ could possibly be constructed. The experimental errors are probably associated with the small sample size; the tiny Pt crucibles contained the sample mass of 30 mg in average, which is rather small for a mixture of granular materials. Therefore, an instrument that allows larger samples will be used for future experiments.

Three sources of potential errors arise from various approximations of the model itself: 1) approximation of the exponential integral as a truncated series, 2) approximation used in the development of Kissinger’s formula, Eq. (2), and 3) shift in $T_m$ caused by peak overlapping. The third issue, the shift in $T_m$, can be seen in Fig. 1 and is illustrated in Fig. 7. As discussed in Appendix A, these approximations have negligible impact on the evaluation of the TGA curves under consideration.

To further verify that Kissinger’s formula provides correct values of $B$ in spite of the $T_m$ shift, we optimized $B_i$s directly from data. Separate fitting to each heating rate with the average values of $A_i$ and $n_i$ and the $w_i$ values listed in Table 7 resulted in fluctuating $B_i$s with averages close to the values from Kissinger’s formula, though with lower standard deviations. Fitting the model to all data for all heating rates at once with the same $A_i$, $n_i$ and the $w_i$ values as for the separate fitting resulted in $B_i$s that were close to both the averages and $B_i$s obtained using Kissinger’s method—see Table 8. Thus, additional fitting did not bring any improvement worth considering.

Because of the compensation effect between $B_i$ and $A_i$ that results from the relatively narrow temperature interval in which the $i^{th}$ reaction starts and is complete, nearly the same fit can be obtained from relatively wide ranges of $B_i$ and $A_i$ combinations [28]. For this reason, Kissinger’s method appears preferable to fitting of $B_i$ and $A_i$ simultaneously. A similar conclusion seems to have been reached by others [30–33, 36].

Conclusions
The kinetic model with empirical reaction order yields a reasonable simulation for the kinetics of multiple overlapping reactions that are typical of melting glass batches. The power-law model employed was successful even though it does not represent the mechanism of reactions between multiple granular solids and ionic and glass-forming melts produced in glass batches at higher temperatures. Thus, each reaction was sufficiently characterized with four coefficients, i.e., the activation energy, the pre-exponential factor, the reaction order, and the weight (the fraction reacted), of which only the weight is a weak function of the rate of heating. To avoid problems with the compensation effect between the activation energy and the pre-exponential factor, we successfully combined Kissinger’s method with least-squares optimization. The three kinetic coefficients plus the reaction weights thus obtained can be used in an advanced model for glass melting in the cold cap.

Acknowledgements

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Appendix A. –Kissinger’s formula

Consider the reaction rate in the form

$$\dot{x} = Af(x)e^{-B/T}$$  \hspace{1cm} (A.1)
where \( f(x) \) is the reaction mechanism function and the dot above the symbol denotes the time derivative. Lists of various \( f(x) \) abound in the literature [31, 35, 37, 39, 40]. If the temperature rises at a constant heating rate, \( \Phi \), then, by setting \( \dot{x} = 0 \), we obtain the formula

\[
\frac{B\Phi}{T_m^2} = -A f'(x_m) e^{-B/T_m}
\]  
(A.2)

where \( f' = df/dx \), and the subscript \( m \) denotes the maximum reaction rate. Introducing the notation \( Y = \Phi/T_m^2 \), \( f_m' = f'(x_m) \), and \( \Theta = 1/T_m \), Eq. (A.2) becomes

\[
BY = -Af_m' e^{-B\Theta}.
\]  
(A.3)

By differentiation with respect to \( \Theta \), we obtain \( dY/d\Theta = -BY(1 + \varepsilon) \), where

\[
\varepsilon = -B^{-1} d \ln(-f_m')/d\Theta.
\]

This equation was derived by Criado and Ortega [39]. Here we have assumed that \( B \) is independent of \( T_m \). This may not be always the case [41]. For example, for diffusion-controlled processes in glasses and polymers, \( B \) is a function of temperature.

Provided that \( x_m \) changes little with \( T_m \), \( \varepsilon \) can be neglected and \( B = -d \ln(Y)/d\Theta \), which is the famous Kissinger formula [27], usually presented as

\[
B = -\left( \frac{\ln \Phi}{T_m^2} \right) \frac{d}{d\left( \frac{1}{T_m} \right)}.
\]  
(A.4)

To prove that \( \varepsilon \ll 1 \), we integrate Eq. (A.1) and use Eq. (A.3) to eliminate \( \Phi \), obtaining
\[ g_m f'_m = -z_m^2 e^{z_m} \int_{z_m}^{\infty} z^{-2} e^{-z} \, dz \]  

(A.6)

where \( g_m = \int_0^{z_m} d(1/f(x)) \) and \( z = B/T \). Using Murray and White’s approximation [37] of the exponential integral, Eq. (A.6) becomes [27]

\[ 2T_m = B(1 + g'_m f'_m). \]  

(A.7)

Based on this equation, recollecting that \( \epsilon = -B^{-1} d\ln(-f_m')/d(1/T_m) \), and with some algebra, one obtains for the \( n^{th} \) order reaction, i.e., \( f(x) = (1-x)^n \), the following expression:

\[ \epsilon = \frac{T_m}{B \left( 1 - \frac{B}{2(1-n)T_m} \right)}. \]  

(A.8)

With \( T_m/B < 0.05 \), \( \epsilon < 0.025 \) for \( 1 < n < 10 \) (see Fig. A1), but it is deduced that Kissinger’s formula fails for large values of \( T_m/B \) and \( n \). The smallness of \( \epsilon \) was asserted for various other reaction mechanisms with \( T_m/B \) small enough by Criado and Ortega [39] who used the approximation by Senum and Yang [42] and concluded that \( \epsilon < 0.05 \) as long as \( B/T_m > 10 \) for commonly used functions \( f(x) \); Senum and Yang approximation differs little from the simpler Murray and White approximation if \( T/B < 0.05 \).

Eq. (A.7) can be used to express \( x_m \) as a function of \( T_m \) for various reaction mechanisms. Fig. A2 shows \( x_m \) for the \( n^{th} \) order reaction as a function of both \( n \) and \( T_m/B \), confirming that \( x_m \) changes little with \( T_m \) for the range of \( T_m/B \) values typical in glass melting.
To explore the effect of overlapping peaks on $B_i$, let us start from Eq. (5) in the form

$$\dot{x} = w_i f_i(x) A_i e^{-B_i/T} + \sum_{j \neq i} w_j \dot{x}_j$$  \hspace{1cm} (A.9)$$

where $\dot{x}_j = w_j f_j(x) A_j e^{-B_j/T}$. Applying to Eq. (A.9) the condition for the $i$th reaction maximum on the TGA curve, i.e., $\ddot{x} = 0$ at each $T = T_{mi}$, we obtain

$$0 = \dot{x}_i(T_{mi}) \left[ \frac{B_i \Phi}{T_{mi}^2} + w_i f_i'(x_{mi}) A_i e^{-B_i/T_{mi}} \right] + \sum_{j \neq i} w_j \dot{x}_j(T_{mi})$$  \hspace{1cm} (A.10)$$

where the prime denotes the derivative. Rearranging and taking a logarithm, Eq. (A.10) becomes

$$\ln \frac{\Phi}{T_{mi}^2} + \ln \left[ 1 + \frac{T_{mi}^2 \sum_{j \neq i} w_j x_j''(T_{mi})}{B_i x_i'(T_{mi})} \right] = \ln \left[ - \frac{w_i f_i'(x_{mi}) A_i}{B_i} \right] - \frac{B_i}{T_{mi}}.$$  \hspace{1cm} (A.11)$$

where $x'' = d^2 x / dT^2$. The Kissinger formula now assumes the form

$$-B_i = \frac{d}{d T_{mi}} \ln \frac{T_{mi}^2 \sum_{j \neq i} w_j x_j''(T_{mi})}{B_i x_i'(T_{mi})}$$

$$-\frac{d}{d T_{mi}} \ln \left[ - \frac{f_i'(x_{mi})}{B_i} \right].$$  \hspace{1cm} (A.12)$$
We have already shown that the third term on the right hand side can be neglected for high-temperature reactions. The second term is negligible if

$$\sum_{j \neq i} w_j x_j^*(T_{mi}) \ll \frac{B_i}{T_{mi}} x_i'(T_{mi}). \quad (A.13)$$

Then Eq. (A.11) becomes Eq. (A.4). If only two peaks overlap, inequality (A.13) reduces to

$$w_j x_j^*(T_{mi}) \ll \frac{B_i}{T_{mi}} x_i'(T_{mi}).$$

Let us check this inequality with peaks 2 and 3 as shown in Fig. 7, where the first maximum associated with reaction 2 (j = 2) is shifted to a higher temperature because of the overlapping peak of reaction 3 (j = 3). With the values $w_3 = 0.054$ and $x_3^*(T_{m2}) = 1.67 \times 10^{-4}$, we get $w_2 x_2^*(T_{m2}) = 9.03 \times 10^{-6}$ K$^{-2}$, with $B_2 = 1.88 \times 10^4$ K, $T_{m2} = 521$ K, and $x_2'(T_{m2}) = 0.665$, we have and $B_2 T_{m2}^{-2} x_2'(T_{m2}) = 4.60 \times 10^{-2}$ K$^{-2}$. Hence, inequality (A.13) is satisfied for this example. It is also likely to be satisfied if the central peak overlaps with two peaks on the opposite sides. Then the two values of $w_j x_j^*(T_{mi})$ of the side peaks have opposite signs.

However, if the neighboring peaks are close to each other and the slope $x_j'' = d x_j'/dT$ at $T = T_{mi}$ is large, inequality (A.13) is not satisfied. As Wilburn [33] showed, it is impossible to determine the kinetic coefficients of such reactions. This may be so, yet any model that simulates the measured data with a sufficient accuracy is suitable for mathematical representation of the response of the reacting mixture to increasing temperature within the realistic rate of heating. Here our objective is practical application of the model for a specific response rather than constructing molecular mechanisms of individual reactions.

Appendix B. –Reaction peaks
For \( f(x) = (1 - x)^n \), the relationship between the peak height and \( T_m \) can be derived from Eqs. (A.1) and (A.2). The resulting expression is:

\[
\frac{d x(T_m)}{dt} = \Phi B \left[ \frac{1}{n} \left( \frac{1}{n} - 1 \right) \frac{2T_m}{B} \right]^{\frac{1}{n-1}}.
\] (B.1)

This expression contains both \( \Phi \) and \( T_m \), but \( T_m \) changes in response to \( \Phi \) according to the formula

\[
\Phi = \frac{AT_m^2}{B} \left[ 1 + (n-1) \frac{2T_m}{B} \exp\left( -\frac{B}{T_m} \right) \right].
\] (B.2)

The line in Fig. B1 plots the peak height, \( dx(T_m)/dt \), against \( T_m \) and \( \Phi \) for peak 3. The data points in Fig. B1 show the heights of deconvoluted peaks (the diamonds) and the heights of the peaks on the TGA curves (the squares). Note that deconvoluted peak heights are located close (virtually on) the line representing formulas (B.1) and (B.2), whereas the points corresponding to the peak heights on the TGA curves are mostly above the lines and somewhat shifted as discussed in Appendix A.

Finally, by using Eq. (A.4), we have

\[
\Phi = \Phi_0 \left( \frac{T_m}{T_{m0}} \right)^2 \exp\left[ -B \left( \frac{1}{T_m} - \frac{1}{T_{m0}} \right) \right].
\] (B.3)

This function is illustrated in Fig. B2. By Eq. (B.3), the relationship between \( T_m \) and \( \Phi \) is independent of the reaction mechanism.
References


Figure captions

Fig. 1 Measured TGA curves for melter feed heated at various rates

Fig. 2 Measured and calculated curves for melter feed heated at 10 K/min for first-order reaction model

Fig. 3 Kissinger plot for melter feed TGA peaks

Fig. 4 Deconvoluted TGA curve for $\Phi = 15$ K/min

Fig. 5 Deconvoluted TGA curve for $\Phi = 5$ K/min

Fig. 6 Measured (solid line) and calculated (dashed line) TGA curves and deconvolution peaks for individual heating rates using average $A_i$ and $n_i$

Fig. 7 Effect of peak overlapping on measured $T_m$

Fig. A1 Error ($\varepsilon$) in $B$ versus $n$ for three values of $T_m/B$ shown legend

Fig. A2 $x_m$ versus $n$ and $T_m/B$ (see legend)

Fig. B1 Peak height as $dx(T_m)/dt$ versus $T_m$ and $\Phi$ ($A = 2.93 \times 10^{10}$ s$^{-1}$, $B = 1.611 \times 10^4$ K, $n = 0.54$)

Fig. B2 $T_m$ versus $\Phi$ for $B = 1.6 \times 10^4$ K and several combinations of $T_{m0}$ and $\Phi_0$ [see Eq. (B3)] as shown in legend
### Table 1. Melter Feed Compositions in g/kg glass (main components)

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<td><strong>Total</strong></td>
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### Table 2. Values of activation energy, \( B_i \), its standard deviation, \( s \), and coefficient of determination, \( R^2 \).

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<th>Peak</th>
<th>( B_i ) [10⁴ K]</th>
<th>( s ) [10⁴ K]</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>2.25</td>
<td>0.18</td>
<td>0.974</td>
</tr>
<tr>
<td>Peak 1A</td>
<td>2.04</td>
<td>0.17</td>
<td>0.973</td>
</tr>
<tr>
<td>Peak 2</td>
<td>1.88</td>
<td>0.06</td>
<td>0.996</td>
</tr>
<tr>
<td>Peak 3</td>
<td>1.61</td>
<td>0.12</td>
<td>0.977</td>
</tr>
<tr>
<td>Peak 4</td>
<td>1.83</td>
<td>0.11</td>
<td>0.986</td>
</tr>
<tr>
<td>Peak 5</td>
<td>4.49</td>
<td>0.32</td>
<td>0.979</td>
</tr>
<tr>
<td>Peak 6</td>
<td>2.98</td>
<td>0.42</td>
<td>0.926</td>
</tr>
<tr>
<td>Peak 7</td>
<td>3.17</td>
<td>0.31</td>
<td>0.962</td>
</tr>
<tr>
<td>Peak 8</td>
<td>2.60</td>
<td>0.60</td>
<td>0.862</td>
</tr>
</tbody>
</table>

### Table 3. Optimized values of \( n_i \), \( w_i \), and \( \log(A_i/s^{-1}) \) for \( \Phi = 15 \text{ K/min} \).

<table>
<thead>
<tr>
<th>Peak</th>
<th>( n_i )</th>
<th>( w_i )</th>
<th>( \log(A_i/s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.73</td>
<td>0.010</td>
<td>20.24</td>
</tr>
<tr>
<td>1A</td>
<td>1.83</td>
<td>0.008</td>
<td>17.09</td>
</tr>
<tr>
<td>2</td>
<td>1.09</td>
<td>0.026</td>
<td>14.06</td>
</tr>
<tr>
<td>3</td>
<td>0.51</td>
<td>0.051</td>
<td>10.49</td>
</tr>
<tr>
<td>4</td>
<td>2.11</td>
<td>0.036</td>
<td>11.57</td>
</tr>
<tr>
<td>5</td>
<td>12.03</td>
<td>0.010</td>
<td>27.94</td>
</tr>
<tr>
<td>6</td>
<td>0.79</td>
<td>0.031</td>
<td>16.96</td>
</tr>
<tr>
<td>7</td>
<td>1.66</td>
<td>0.003</td>
<td>17.32</td>
</tr>
<tr>
<td>8</td>
<td>3.44</td>
<td>0.016</td>
<td>12.93</td>
</tr>
</tbody>
</table>

### Table 4. Values of \( \log(A_i/s^{-1}) \), average values, standard deviations, and relative standard deviations (RSD) for Peaks 1–8.

<table>
<thead>
<tr>
<th>( \Phi ) [K min⁻¹]</th>
<th>1</th>
<th>1A</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.28</td>
<td>16.93</td>
<td>13.98</td>
<td>10.41</td>
<td>11.53</td>
<td>28.02</td>
<td>16.70</td>
<td>17.24</td>
<td>12.41</td>
</tr>
<tr>
<td>5</td>
<td>20.35</td>
<td>17.16</td>
<td>14.05</td>
<td>10.54</td>
<td>11.57</td>
<td>28.04</td>
<td>16.98</td>
<td>17.26</td>
<td>12.79</td>
</tr>
<tr>
<td>10</td>
<td>20.15</td>
<td>17.05</td>
<td>14.03</td>
<td>10.34</td>
<td>11.36</td>
<td>28.37</td>
<td>17.08</td>
<td>17.41</td>
<td>12.67</td>
</tr>
<tr>
<td>15</td>
<td>20.24</td>
<td>17.09</td>
<td>14.06</td>
<td>10.49</td>
<td>11.57</td>
<td>27.94</td>
<td>16.96</td>
<td>17.32</td>
<td>12.93</td>
</tr>
<tr>
<td>20</td>
<td>20.17</td>
<td>17.01</td>
<td>14.03</td>
<td>10.52</td>
<td>11.64</td>
<td>27.95</td>
<td>16.81</td>
<td>17.33</td>
<td>12.85</td>
</tr>
<tr>
<td>50</td>
<td>20.34</td>
<td>17.07</td>
<td>14.01</td>
<td>10.47</td>
<td>11.41</td>
<td>28.09</td>
<td>16.85</td>
<td>17.37</td>
<td>12.52</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>20.26</td>
<td>17.05</td>
<td>14.03</td>
<td>10.46</td>
<td>11.51</td>
<td>28.07</td>
<td>16.90</td>
<td>17.32</td>
<td>12.69</td>
</tr>
<tr>
<td><strong>Stdev</strong></td>
<td>0.08</td>
<td>0.07</td>
<td>0.03</td>
<td>0.07</td>
<td>0.10</td>
<td>0.14</td>
<td>0.12</td>
<td>0.06</td>
<td>0.18</td>
</tr>
<tr>
<td><strong>RSD</strong></td>
<td>0.004</td>
<td>0.002</td>
<td>0.007</td>
<td>0.009</td>
<td>0.005</td>
<td>0.007</td>
<td>0.003</td>
<td>0.014</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Values of $n_i$, average values, standard deviations (values in parentheses were not included), and relative standard deviations for Peaks 1–8.

<table>
<thead>
<tr>
<th>$\Phi$ [K min$^{-1}$]</th>
<th>1</th>
<th>1A</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.00</td>
<td>1.90</td>
<td>0.71</td>
<td>0.39</td>
<td>3.39</td>
<td>(1.19)</td>
<td>1.81</td>
<td>(0.10)</td>
<td>2.05</td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
<td>2.00</td>
<td>0.93</td>
<td>0.62</td>
<td>2.23</td>
<td>(0.61)</td>
<td>1.00</td>
<td>1.29</td>
<td>3.13</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>1.32</td>
<td>1.30</td>
<td>0.56</td>
<td>1.79</td>
<td>2.00</td>
<td>0.95</td>
<td>2.00</td>
<td>5.31</td>
</tr>
<tr>
<td>15</td>
<td>2.00</td>
<td>1.99</td>
<td>1.09</td>
<td>0.50</td>
<td>2.37</td>
<td>2.00</td>
<td>1.58</td>
<td>1.15</td>
<td>3.59</td>
</tr>
<tr>
<td>20</td>
<td>2.00</td>
<td>2.00</td>
<td>1.08</td>
<td>0.57</td>
<td>2.42</td>
<td>2.00</td>
<td>1.78</td>
<td>(0.55)</td>
<td>4.70</td>
</tr>
<tr>
<td>50</td>
<td>2.00</td>
<td>2.00</td>
<td>1.23</td>
<td>0.61</td>
<td>1.04</td>
<td>2.00</td>
<td>2.66</td>
<td>0.90</td>
<td>4.41</td>
</tr>
<tr>
<td>Average</td>
<td>2.00</td>
<td>1.87</td>
<td>1.06</td>
<td>0.54</td>
<td>2.21</td>
<td>2.00</td>
<td>1.63</td>
<td>1.33</td>
<td>3.87</td>
</tr>
<tr>
<td>Stdev</td>
<td>0.00</td>
<td>0.27</td>
<td>0.21</td>
<td>0.08</td>
<td>0.77</td>
<td>0.00</td>
<td>0.63</td>
<td>0.47</td>
<td>1.18</td>
</tr>
<tr>
<td>RSD</td>
<td>0.00</td>
<td>0.14</td>
<td>0.20</td>
<td>0.15</td>
<td>0.35</td>
<td>0.00</td>
<td>0.39</td>
<td>0.35</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 6. Values of $w_i$ and the total fraction reacted, $w = \Sigma w_i$, for Peaks 1–8.

<table>
<thead>
<tr>
<th>$\Phi$ [K min$^{-1}$]</th>
<th>1</th>
<th>1A</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.009</td>
<td>0.008</td>
<td>0.026</td>
<td>0.052</td>
<td>0.041</td>
<td>0.000</td>
<td>0.045</td>
<td>0.000</td>
<td>0.018</td>
<td>0.198</td>
</tr>
<tr>
<td>5</td>
<td>0.007</td>
<td>0.011</td>
<td>0.027</td>
<td>0.055</td>
<td>0.037</td>
<td>0.000</td>
<td>0.034</td>
<td>0.015</td>
<td>0.022</td>
<td>0.207</td>
</tr>
<tr>
<td>10</td>
<td>0.008</td>
<td>0.007</td>
<td>0.031</td>
<td>0.049</td>
<td>0.031</td>
<td>0.002</td>
<td>0.023</td>
<td>0.028</td>
<td>0.023</td>
<td>0.203</td>
</tr>
<tr>
<td>15</td>
<td>0.008</td>
<td>0.010</td>
<td>0.025</td>
<td>0.051</td>
<td>0.038</td>
<td>0.001</td>
<td>0.036</td>
<td>0.009</td>
<td>0.023</td>
<td>0.202</td>
</tr>
<tr>
<td>20</td>
<td>0.008</td>
<td>0.010</td>
<td>0.023</td>
<td>0.049</td>
<td>0.040</td>
<td>0.003</td>
<td>0.042</td>
<td>0.002</td>
<td>0.025</td>
<td>0.203</td>
</tr>
<tr>
<td>50</td>
<td>0.007</td>
<td>0.012</td>
<td>0.024</td>
<td>0.055</td>
<td>0.026</td>
<td>0.010</td>
<td>0.050</td>
<td>0.005</td>
<td>0.013</td>
<td>0.201</td>
</tr>
</tbody>
</table>

Table 7. Values of $w_i$ based on the average values of $A_i$ and $n_i$ listed in Tables 4 and 5, $w = \Sigma w_i$, and the total fractional mass loss as measured by TGA, $w_{TGA}$.

<table>
<thead>
<tr>
<th>$\Phi$ [K min$^{-1}$]</th>
<th>1</th>
<th>1A</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>w</th>
<th>$w_{TGA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.008</td>
<td>0.007</td>
<td>0.027</td>
<td>0.054</td>
<td>0.033</td>
<td>0.000</td>
<td>0.036</td>
<td>0.009</td>
<td>0.027</td>
<td>0.201</td>
<td>0.195</td>
</tr>
<tr>
<td>5</td>
<td>0.008</td>
<td>0.010</td>
<td>0.030</td>
<td>0.054</td>
<td>0.035</td>
<td>0.000</td>
<td>0.046</td>
<td>0.002</td>
<td>0.026</td>
<td>0.210</td>
<td>0.206</td>
</tr>
<tr>
<td>10</td>
<td>0.007</td>
<td>0.009</td>
<td>0.027</td>
<td>0.041</td>
<td>0.045</td>
<td>0.001</td>
<td>0.037</td>
<td>0.008</td>
<td>0.027</td>
<td>0.202</td>
<td>0.196</td>
</tr>
<tr>
<td>15</td>
<td>0.008</td>
<td>0.011</td>
<td>0.026</td>
<td>0.054</td>
<td>0.034</td>
<td>0.003</td>
<td>0.038</td>
<td>0.010</td>
<td>0.022</td>
<td>0.203</td>
<td>0.199</td>
</tr>
<tr>
<td>20</td>
<td>0.008</td>
<td>0.011</td>
<td>0.024</td>
<td>0.053</td>
<td>0.034</td>
<td>0.003</td>
<td>0.036</td>
<td>0.010</td>
<td>0.022</td>
<td>0.200</td>
<td>0.197</td>
</tr>
<tr>
<td>50</td>
<td>0.008</td>
<td>0.011</td>
<td>0.023</td>
<td>0.049</td>
<td>0.040</td>
<td>0.005</td>
<td>0.031</td>
<td>0.014</td>
<td>0.020</td>
<td>0.201</td>
<td>0.197</td>
</tr>
</tbody>
</table>

Table 8. Values of $B_i$ [$10^4$ K] optimized for average reaction orders and pre-exponential factors.

<table>
<thead>
<tr>
<th>Peak</th>
<th>1</th>
<th>1A</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kissinger</td>
<td>2.25</td>
<td>2.04</td>
<td>1.88</td>
<td>1.61</td>
<td>1.83</td>
<td>4.49</td>
<td>2.98</td>
<td>3.17</td>
<td>2.60</td>
</tr>
<tr>
<td>Fit to all data</td>
<td>2.25</td>
<td>2.04</td>
<td>1.87</td>
<td>1.61</td>
<td>1.83</td>
<td>4.52</td>
<td>2.98</td>
<td>3.17</td>
<td>2.59</td>
</tr>
<tr>
<td>Average of separate fits</td>
<td>2.25</td>
<td>2.04</td>
<td>1.88</td>
<td>1.61</td>
<td>1.83</td>
<td>4.50</td>
<td>2.99</td>
<td>3.17</td>
<td>2.59</td>
</tr>
<tr>
<td>StDev</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. A1.
Fig. A2.
Fig. B1.
Fig. B2.