

Analytic method for determining the activation energy of sintering using the master sintering curve approach

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Analytic expressions have been developed to determine the activation energy of sintering using the Master Sintering Curve methodology. The analytical equations lead to values of the activation energy within 1% of the true value, whether noise is present in the data or not. The analytic expressions can further be used to discriminate between alternative kinetic models and to determine the pre-exponential factor. The origin of the accuracy of the analytical expressions is also discussed.

Key words: Master sintering curve, Sintering, Activation energy, Pre-exponential factor.

Introduction

The sintering of ceramic powders is an Arrhenius-type kinetic process, and three types of terms customarily appear in the rate expression for sintering: a pre-exponential factor, an exponential term containing the activation energy, and a third term which accounts for the dependence of the rate on the spatial distribution of matter. Rate equations for sintering can take numerous forms depending on the underlying mechanism and degree of complexity treated [1, 2]. To describe the rate of sintering, it is desired to have accurate values or expressions for all three terms appearing in the rate equation over the full range of density changes, although in practice this is often not achieved. When it is not possible to determine all aspects of the rate expression, a value of the activation energy often suffices, which can then serve as a basis for comparing the sintering kinetics of different materials.

To obtain the activation energy of sintering, two standard types of experiments can be conducted, namely, isothermal and non-isothermal studies. The rate data versus time from either of these experiments can then be analyzed by either differential or integral methods of kinetic analysis [3]. Typically, a mechanism or model is assumed, from which the goodness of fit between the kinetic data and assumed mechanism is then used to determine rate constants; a plot of the logarithm of the rate constant versus reciprocal temperature then leads to regions of linear behavior from which the activation energy can be determined.

One shortcoming to these approaches is that a closed

form mechanistic description is often desired. For elementary steps in gas-phase or liquid-phase kinetics [3-5], such mechanisms are straightforward to postulate. For heterogeneous or solid-state kinetic processes, especially the latter for which diffusion may play a role, more complex mechanisms may need to be invoked. Even for solid state reactions, however, closed form expressions for mechanistic testing are available for idealized types of reactions [6-8], such as for diffusion control, phase boundary control, and nucleation and growth.

For the specific case of sintering, however, the spatial changes of matter during the process preclude a simple, closed form kinetic expression over a wide range of density. To circumvent this difficulty, the Master Sintering Curve (MSC) approach [9], a widely used integral method [10-26], has been developed to characterize the sintering process. With the MSC method, dilatometer data obtained at different heating rates are used to determine the activation energy of sintering without having to prescribe specifically the functional form of an underlying mechanism. The underlying mechanism (or unknown function) is then represented in terms of a graph. With this procedure, however, an integral appears which cannot be solved analytically, and thus numerical integration is required.

In this work, we develop an approximate analytical expression to evaluate accurately this integral. We also illustrate how the analytical expression can be used to discriminate between alternative postulated kinetic mechanisms of sintering and to determine the pre-exponential factor.

Theory

The MSC approach [9] is an integral kinetic method for obtaining the activation energy of sintering and is

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based on the combined stage sintering model [27], which treats shrinkage during sintering as arising from mass transfer due to two diffusion processes, namely grain boundary and volume diffusion. Changes in length, L , that occur during sintering are given as a linearly additive sum of the two diffusional processes as:

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{k_b T} \left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4} \right) \quad (1)$$

where t is the time, γ is the surface energy, Ω is the atomic volume, k_b is the Boltzmann constant, T is the absolute temperature, and G is the mean grain diameter. The coefficients for volume (subscript v) and grain boundary diffusion (subscript b) are, respectively, D_v and D_b , and δ is the average width of a grain boundary. The Γ_i quantities, which depend on density but not on the heating schedule, are lumped scaling functions in terms of the mean grain diameter which relate driving forces, mean diffusion distances, and other microstructural aspects that influence the sintering rate.

Because the quantities Γ_i and G are functions alone of microstructure or relative density, ρ , Eq. 1 can be rearranged so that one side, $\Phi(\rho)$, contains all the properties dependant on density whereas the other side, $\Theta[T(t)]$, depends only on the heating schedule and activation energy. Provided sintering is dominated by a single mechanism, either volume or grain boundary diffusion, the factoring of Eq. 1 in this manner leads to:

$$\Phi(\rho) = \Theta[T(t)] \quad (2)$$

with:

$$\Phi(\rho) = \frac{k_b}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n}{3\rho\Gamma(\rho)} d\rho \quad (3)$$

$$\Theta[T(t)] = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (4)$$

In these equations, D_0 is the pre-exponential factor for diffusion, Q is the activation energy, and R is the universal gas constant. The exponent n is 3 or 4 for volume or grain boundary diffusion, respectively. Due to the underlying assumptions, Eqs. 2-4 are only valid when the microstructural evolution is dependent on density alone, which is most valid during sintering for relative densities in the range of 0.6 to 0.9.

The functional relationship between ρ and $\Phi(\rho)$ is the MSC, which is unique for each powder and green forming method, including a fixed green density. Since Eq. 4 depends on time and temperature, both of which are simple to monitor in an experiment, $\Theta[T(t)]$ is known if Q is known or can be approximated. The

equality in Eq. 2 can then be used to obtain the value of $\Phi(\rho)$ without determining the individual factors comprising Eq. 3 or making any further assumptions. When $\ln[\Theta[T(t)]]$ is plotted versus ρ for sintering data collected at different heating rates, the separate curves will collapse to a single curve only if the true activation energy has been established.

For a linear heating rate, β , the temperature evolves as $T = T_0 + \beta t$ where T_0 is the initial temperature, and thus $\beta = dT/dt$ which leads to:

$$\Theta[T(t)] = \int_{T_0}^T \frac{1}{\beta T} \exp\left(-\frac{Q}{RT}\right) dT \quad (5)$$

We note that in the original MSC method, the activation energy in Eq. 5 is obtained numerically. In addition to sintering, the MSC approach can be applied to other thermally activated processes when the mechanism is unknown [28], provided that the thermally activated process has a single activation energy and is independent of the heating profile.

Prior to the development of the MSC method for determining the activation energy of sintering, Lee and Beck [29] had analyzed the kinetics of coal decomposition obtained by thermogravimetric analysis. The kinetics of solid decomposition were represented with an Arrhenius-type expression of the form:

$$\frac{d\rho}{dT} = \frac{A'}{\beta} \exp\left(-\frac{Q}{RT}\right) \phi'(\rho) \quad (6)$$

where A' is the pre-exponential factor, ρ is the decomposed fraction of solid (the conversion), and $\phi'(\rho)$ is a function which depends on the reaction mechanism. Integration of Eq. 6 between the initial and final temperatures and conversions yields:

$$\begin{aligned} \frac{\beta}{A'} \int_{\rho_0}^{\rho} \frac{d\rho}{\phi'(\rho)} &= \Theta[T(t)] = \int_{T_0}^T \exp\left(-\frac{Q}{RT}\right) dT \\ &= \frac{RT^2}{Q} \exp\left(-\frac{Q}{RT}\right) \Big|_{T_0}^T - \int_{T_0}^T \frac{2RT}{Q} \exp\left(-\frac{Q}{RT}\right) dT \end{aligned} \quad (7)$$

The right-hand side of Eq. 7 is the result of integration by parts and leads to the same integral of the exponential function in Q , which cannot be evaluated analytically. By rearranging the terms containing Q in Eq. 7 and grouping the integrals together, one obtains:

$$\int_{T_0}^T \left(1 + \frac{2RT}{Q}\right) \exp\left(-\frac{Q}{RT}\right) dT = \frac{RT^2}{Q} \exp\left(-\frac{Q}{RT}\right) \Big|_{T_0}^T \quad (8)$$

For moderate temperatures and large activation energies, $2RT/Q$ is far less than unity, and $(1 + 2RT/Q)$ is approximately equal to one and therefore approximately constant. Upon factoring $(1 + 2RT/Q)$ from the integral, one obtains:

$$\Phi'(\rho) = \int_{\rho_0}^{\rho} \frac{d\rho}{\phi'(\rho)} = \frac{A'}{\beta} \left[\frac{\left(\frac{RT^2}{Q}\right) \exp\left(-\frac{Q}{RT}\right)}{\left(1 + \frac{2RT}{Q}\right)} - \frac{\left(\frac{RT_0^2}{Q}\right) \exp\left(-\frac{Q}{RT_0}\right)}{\left(1 + \frac{2RT_0}{Q}\right)} \right] \\ \equiv \frac{A'}{\beta} (\lambda_T - \lambda_{T_0}) \quad (9)$$

where λ_T and λ_{T_0} denote the two terms in square brackets. Equation 9 can thus be used with a kinetic mechanism or model to directly find the activation energy of sintering; some common kinetic models and their integrated forms are shown in Table 1.

Equation 9 can be further approximated if, when compared to λ_T , the value of λ_{T_0} is assumed to be small (which is often the case for T_0 moderately removed from T and for large activation energies) as:

$$\Phi'(\rho) = \frac{A'}{\beta} \lambda_T = \frac{A'}{\beta} \frac{\left(\frac{RT^2}{Q}\right) \exp\left(-\frac{Q}{RT}\right)}{\left(1 + \frac{2RT}{Q}\right)} \quad (10)$$

which can be rearranged to:

$$\ln\left[\frac{\Phi'(\rho)}{T^2}\right] = \ln\left[\frac{A'R}{\beta(Q + 2RT)}\right] - \frac{Q}{RT} \quad (11)$$

If the correct mechanism is known, then $\ln[\Phi'(\rho)/T^2]$ plotted versus $1/T$ yields linear behavior, and the slope is equal to $-Q/R$. The pre-exponential factor can then be obtained from either the intercept or by using the value of Q with Eq. 11 to obtain A' at each value of T and then averaging these. This summarizes the method of Lee and Beck [29], which affords a means to obtain values of A' and Q when the kinetic

mechanism is known.

The contribution of this study is to use the approximation developed for the integral above to obtain the activation energy of sintering analytically, instead of numerically as is typically done. We note, however, that Eq. 5 has a $1/T$ term not present in Eq. 7, and thus the above method must be modified as follows [30]. Integration by parts applied to Eq. 5 yields:

$$\Theta[T(t)] = \frac{1}{\beta} \int_{T_0}^T \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dT \\ = \frac{1}{\beta} \left(\frac{1}{T} \int_{T_0}^T \exp\left(-\frac{Q}{RT}\right) dT - \int_{T_0}^T \left[\int_{T_0}^T \exp\left(-\frac{Q}{RT}\right) dT \right] \left(-\frac{1}{T^2}\right) dT \right) \quad (12)$$

where the integral containing the exponential function now appears twice. Upon using Eq. 9 followed by rearrangement one obtains the final analytic expression:

$$\Theta[T(t)] \\ = \frac{1}{\beta} \left(\frac{\left(\frac{RT}{Q}\right) \exp\left(-\frac{Q}{RT}\right)}{\left(1 + \frac{2RT}{Q}\right)} + \left[\frac{\left(\frac{RT^2}{Q}\right) \exp\left(-\frac{Q}{RT}\right)}{\left(1 + \frac{2RT}{Q}\right)} - \frac{\left(\frac{RT_0^2}{Q}\right) \exp\left(-\frac{Q}{RT_0}\right)}{\left(1 + \frac{2RT_0}{Q}\right)} \right] \frac{R}{(Q + 2RT)} \right) \quad (13)$$

or in simplified form as:

$$\Theta[T(t)] = \frac{1}{\beta} \left(\frac{\lambda_T}{T} + (\lambda_T - \lambda_{T_0}) \frac{R}{Q} \frac{1}{(1 + 2RT/Q)} \right) \quad (14)$$

All the equations for the master sintering curve can now be summarized as:

$$\frac{k_p}{\gamma \Omega D_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n}{\rho \Gamma(\rho)} d\rho \equiv \Phi(\rho) = \Theta[T(t)] \\ \equiv \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \approx \frac{1}{\beta} \left(\frac{\lambda_T}{T} + (\lambda_T - \lambda_{T_0}) \frac{R}{Q} \frac{1}{(1 + 2RT/Q)} \right) \quad (15)$$

We next illustrate how the approximation for the integral containing the exponential allows one to obtain Q analytically instead of numerically.

Results

To demonstrate the use of Eq. 15, density versus

Table 1. Kinetic mechanisms $\phi'(\rho)$ with their integrated forms $\Phi'(\rho) = \int_{\rho_0}^{\rho} d\rho / \phi'(\rho)$.

Kinetic Model	$\phi'(\rho)$	$\Phi'(\rho)$
2-D Phase boundary movement	$2(1-\rho)^{1/2}$	$1-(1-\rho)^{1/2}$
Valensi Diffusion	$1/[-\ln(1-\rho)]$	$(1-\rho)\ln(1-\rho) + \rho$
Parabolic Diffusion	$1/\rho$	$\rho^2/2$
First order	$(1-\rho)^1$	$-\ln(1-\rho)$
Second order	$(1-\rho)^2$	$1/(1-\rho)$

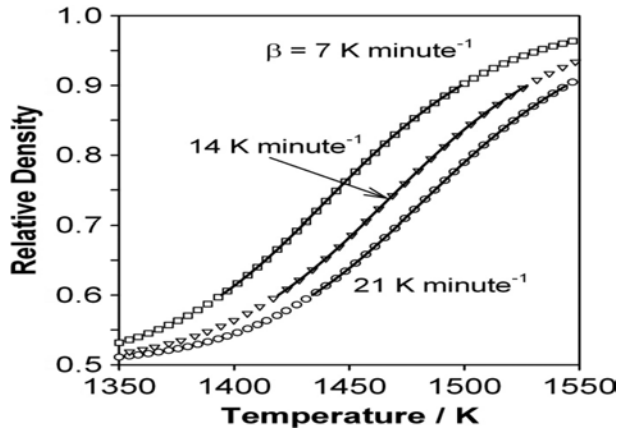


Fig. 1. Relative density data (symbols) versus temperature simulated from second order kinetics at three heating rates with $Q = 450 \text{ kJ mol}^{-1}$ and $A = 10^{19} \text{ K minute}^{-1}$, the fifth order polynomial fit is shown by lines.

temperature data were simulated at three linear heating rates of $\beta = 7, 14, \text{ and } 21 \text{ }^{\circ}\text{C minute}^{-1}$ at three activation energies of $Q = 250, 450, \text{ and } 650 \text{ kJ mol}^{-1}$ with a pre-exponential factor $A = 10^{19} \text{ K minute}^{-1}$. These data were generated for the case of second order kinetics by numerical integration of:

$$\frac{1}{1-\rho} - \frac{1}{1-\rho_0} = \int_{T_0}^T \frac{A}{\beta T} \exp\left(-\frac{Q}{RT}\right) dT \quad (16)$$

Fig. 1 shows as an example the three curves generated for $Q = 450 \text{ kJ mol}^{-1}$; the shape of these curves is qualitatively similar to the density profiles obtained in sintering experiments. We note that to arrive at Eq. 16, the pre-exponential factor A' in Eq. 6 has been replaced with $A' = A/T$ in order to obtain the form of the temperature dependence in the integral appearing in the MSC method (Eq. 5).

Values of $\ln[\Theta(T(t))]$ for each density-versus-temperature data set were then calculated with the three different equations given below:

$$\ln[\Theta(T(t))] = \ln\left[\int_{T_0}^T \frac{1}{\beta T} \exp\left(-\frac{Q}{RT}\right) dT\right] \quad (17)$$

$$\ln[\Theta(T(t))] = \ln\left[\frac{1}{\beta} \left(\frac{\lambda_T}{T} + (\lambda_T - \lambda_{T_0}) \frac{R}{Q(1 + 2RT/Q)}\right)\right] \quad (18)$$

$$\ln[\Theta(T(t))] = \ln\left[\frac{\ln \frac{T}{T_0}}{\beta(T - T_0)} (\lambda_T - \lambda_{T_0})\right] \quad (19)$$

Equation 17 was integrated numerically using the trapezoidal rule with step sizes of 0.01, 0.001 and

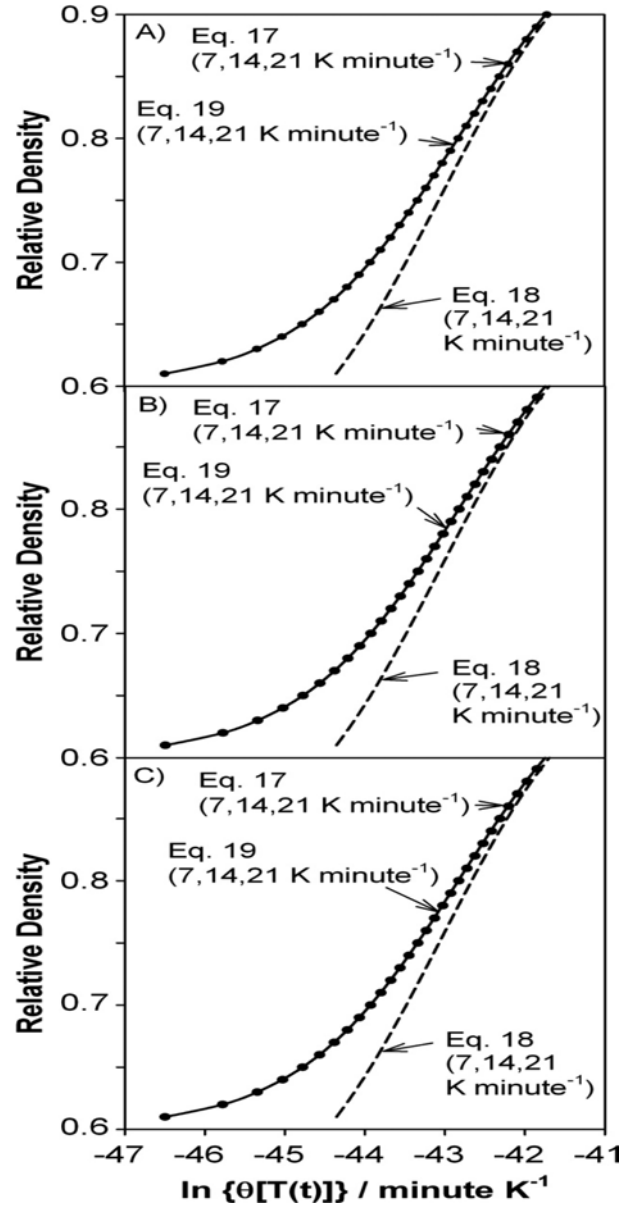


Fig. 2. Master sintering curves simulated from second order density-temperature data with $A = 10^{19} \text{ K minute}^{-1}$ for A) $Q = 250 \text{ kJ mol}^{-1}$, B) $Q = 450 \text{ kJ mol}^{-1}$, and c) $Q = 650 \text{ kJ mol}^{-1}$. In each panel, nine curves are shown representing three heating rates which were analyzed with Eq. 17 (symbols), Eq. 18 (dashed lines), and Eq. 19 (solid lines). The result from Eqs. 17 and 19 are virtually indistinguishable from each other.

0.0001 relative density. For the simulations generated with an activation energy of 450 kJ mol^{-1} , the difference in calculated activation energies between the three step sizes was less than $0.0003 \text{ kJ mol}^{-1}$ and thus a step size of 0.01 is used for all numerical integrations. In the second approach as given by Eq. 18, the analytic expression in Eq. 14 was used with Eq. 17. Equation 19 was obtained by replacing the $1/T$ quantity in Eq. 17 with a logarithmic mean value that could then be removed from the integral, thereby allowing for use of Eq. 9 to represent the integral.

For each of the three equations used to represent

Table 2. Activation energies determined by the three equations for different input Q values with second order kinetics and $A = 10^{19} \text{ K minute}^{-1}$.

Input Q value (kJ mol ⁻¹)	Q from Eq. 17 (kJ mol ⁻¹)	Q from Eq. 18 (kJ mol ⁻¹)	Q from Eq. 19 (kJ mol ⁻¹)
250	250.00	250.05	249.98
450	449.97	450.10	449.94
650	650.00	650.14	649.94

$\Theta[T(t)]$, the same procedure for determining the activation energy was followed. First, the simulated temperature-density data were fitted to a fifth order polynomial over the range of $\rho = 0.6$ to $\rho = 0.9$ so that temperature and $\Theta[T(t)]$ values could be directly compared at discrete values of ρ at the different heating rates. The absolute values of the differences in $\ln[\Theta[T(t)]]$ at the different heating rates were next summed, and then the Q values for each equation were varied using a generalized reduced gradient nonlinear optimization code until the sum reached a minimum.

Fig. 2 shows the MSCs calculated by the three methods at the three heating rates for each activation energy, *i.e.*, there are nine curve in each panel. For each method, namely Eqs. 17-19, the data at the three heating rates collapse to a single curve. In addition, the curves obtained from Eqs. 17 and 19 are virtually indistinguishable whereas the curves obtained from Eq. 18 are offset relative to the other two at each relative density. Table 2 compares the original Q values used to simulate the data with the calculated Q values determined from Eqs. 17-19. Not surprisingly, numeric integration (Eq. 17) produced the most accurate results, in part because the equation involves no approximation and thus the degree of accuracy depends only on the step size used. Both approximate analytic equations were also able to produce activation energies within 0.08% of the input value. In addition, even though the curves in Fig. 2 from Eq. 18 are different from the curves for the other two methods, the activation energies are nearly the same for all cases.

To assess further the utility of the analytical equations presented above, density data with $\pm 2\%$ random noise versus temperature were generated, as shown in Fig. 3. These curves were next analyzed using Eqs. 17-19 after fitting the noisy data to a fifth order polynomial; the results for the Q values with and without noise are summarized in Table 3. In all instances, the activation energies determined were within $\sim 1\%$ of the value of $Q = 450 \text{ kJ mol}^{-1}$ used to generate the data. Once again, the MSC curves (not shown here) generated by Eqs. 17 and 19 agreed well with each other. The data in Table 3 thus indicate that the analytical expressions derived in this work are robust enough to use on real data which has noise.

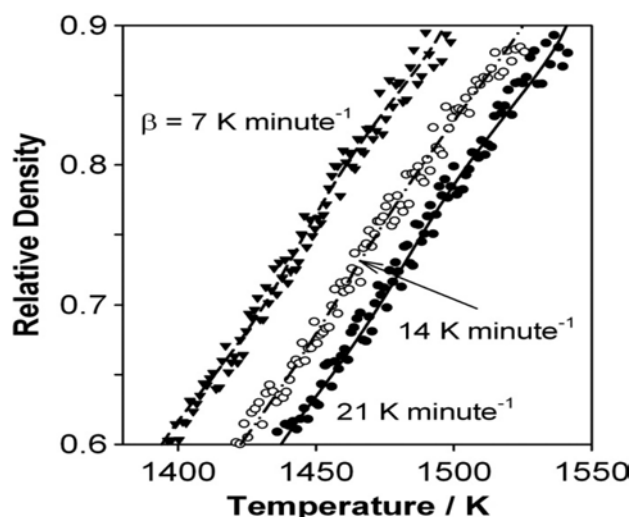


Fig. 3. Relative density data with $\pm 2\%$ noise versus temperature simulated from second order kinetics with $A = 10^{19} \text{ K minute}^{-1}$ and $Q = 450 \text{ kJ mol}^{-1}$; the fifth order polynomial fit is shown by lines.

Table 3. Activation energies determined for density data simulated with and without 2% noise with $Q = 450 \text{ kJ mol}^{-1}$ with second order kinetics and $A = 10^{19} \text{ K minute}^{-1}$.

	Q from Eq. 17 (kJ mol ⁻¹)	Q from Eq. 18 (kJ mol ⁻¹)	Q from Eq. 19 (kJ mol ⁻¹)
Without Noise	449.97	450.10	449.94
With $\pm 2\%$ Noise	456.90	445.09	456.83

To summarize to this point, we note that the MSC approach is a useful integral method of kinetic analysis because no knowledge of the functional form of the underlying kinetic mechanism or model is required. Both of the analytical equations presented herein reproduce the activation energies to a high degree of accuracy and Eq. 19 is especially useful in that it also quite accurately reproduces the shape of the MSC profile. In principle, then, the analytical equations reproduce not only the expression for $\Theta[T(t)]$, namely the value of the integral needed to determine the activation energy, but also the expression for $\Phi(\rho)$, namely the value of the integral of the underlying kinetic mechanism. Thus, as kinetic models or mechanisms become available for describing the kinetics of sintering via the evolution of density, such models can be tested for accuracy via the analytical equations presented here.

As an example of this, density versus temperature data were simulated for a given Q and A with a second order mechanism. These data were next analyzed with Eq. 19, which contains no assumptions about the underlying kinetic mechanism, to determine Q via $\Theta[T(t)]$, which is equal to $\Phi(\rho)$ and also to $\Phi'(\rho)/A$ due to the different factoring of terms in the MSC method (Eqs. 2-4) as compared to that of Lee and Beck [29] in Eq. 7. We next use assumed forms of $\Phi'(\rho)$ to simultaneously discriminate between

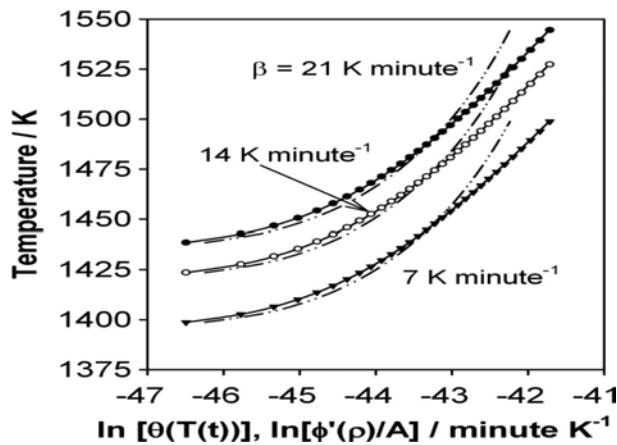


Fig. 4. Temperature versus $\ln[\Theta(T(t))]$ (symbols) obtained from data simulated from second order kinetics at three heating rates with $Q = 450 \text{ kJ mol}^{-1}$ and $A = 10^{19} \text{ K minute}^{-1}$. Comparison of temperature versus $\ln[\Phi'(\rho)/A]$ and for first order (dashed lines) and second order (solid lines) mechanisms.

postulated alternative mechanisms and to determine A via the goodness of fit. For example, if it is assumed that the underlying kinetics are either first order or second order, then plots of $\ln[\Phi'(\rho)/A]$ versus temperature can be prepared. As seen in Fig. 4, the relationship between $\ln[\Theta(T(t))]$ and $\ln[\Phi'(\rho)/A]$ versus temperature is well described for a second order mechanism, and the determined value of A is $9.9 \times 10^{18} \text{ K minute}^{-1}$, which is close to the input value of $10^{19} \text{ K minute}^{-1}$. For a first order mechanism, however, $\ln[\Theta(T(t))]$ and $\ln[\Phi'(\rho)/A]$ are not in as good agreement, and the value of $A = 3.1 \times 10^{18} \text{ K minute}^{-1}$ is also larger in error. Thus, the analytical expressions developed in this work can be used to help discriminate between competing mechanisms and to determine pre-exponential factors, as is often done in kinetic analysis.

The analytical equations presented above also afford another method to discriminate between competing mechanisms and to determine the pre-exponential factor. This approach relies on the more traditional graph of rate data versus reciprocal temperature and then checking for linear behavior. To perform this analysis, we follow the procedure outlined by Eqs. 10 and 11, but now use Eq. 19 without the λ_0 term to describe $\Phi'(\rho)$; after algebraic re-arrangement this yields:

$$\ln \left[\frac{\Phi'(\rho)(T - T_0)}{(\ln T - \ln T_0)T^2} \right] = \ln \left[\frac{AR}{\beta(Q + 2RT)} \right] - \frac{Q}{RT} \quad (20)$$

When the left-hand side is graphed versus $1/T$, the slope of the equation is given by $-Q/R$. Fig. 5A demonstrates this linear behavior for density data simulated for second order kinetics with $Q = 450 \text{ kJ mol}^{-1}$ and $A = 10^{19} \text{ K minute}^{-1}$ and then analyzed with $\Phi'(\rho)$ given by a second order mechanism. As shown in Table 4, this graphical method of analysis leads to a value of Q within approximately 1% of the value

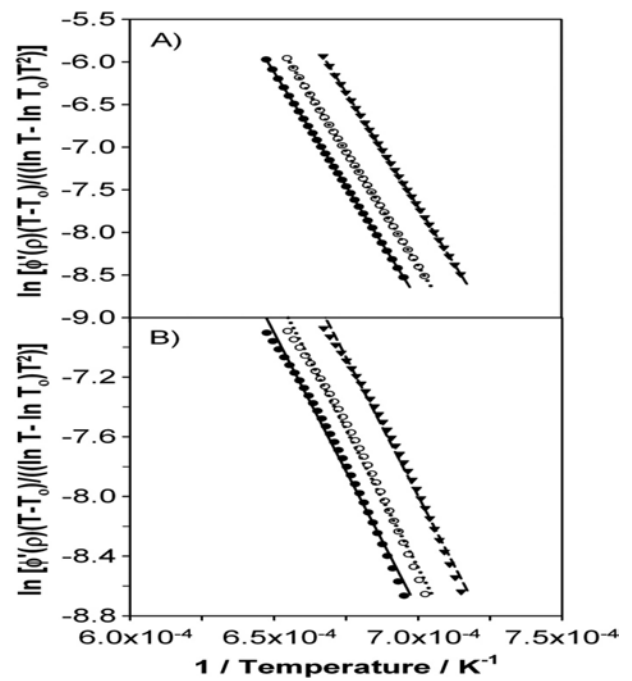


Fig. 5. Graphical analysis with Eq. 20 for A) second order and B) first order mechanisms for data simulated from second order kinetics at three heating rates with $Q = 450 \text{ kJ mol}^{-1}$ and $A = 10^{19} \text{ K minute}^{-1}$.

Table 4. Activation energies and pre-exponential factors determined from analysis of simulated data using $Q = 450 \text{ kJ mol}^{-1}$ with second order kinetics and $A = 10^{19} \text{ K minute}^{-1}$.

Assumed Mechanism	Q (kJ mol^{-1})	A (K minute^{-1})
First Order	308.7 ± 0.2	$2.22 \pm 0.3 \times 10^{13}$
Second Order	445.2 ± 0.1	$3.45 \pm 0.01 \times 10^{18}$

used to simulate the data. The resulting pre-exponential, obtained from the intercept or from averaging the values of A obtained from Eq. 20, is of the correct order of magnitude and is within 65% of the input value. If the incorrect mechanism for $\Phi'(\rho)$ is assumed, however, non-linear behavior results (see Fig. 5B) and both the activation energy and the pre-exponential factor (see Table 4) are much more inaccurate as compared to the input values. The results embodied by Fig. 4 and Table 3 versus those in Fig. 5 and Table 4 indicate that the former is the preferred method as more accurate results are obtained. The poorer accuracy in A arising from the latter method presumably occurs due to neglect of the λ_0 term; this approximation was used to obtain Eq. 20 in a form suitable for linear analysis.

Discussion

In this work, expressions have been derived to obtain analytically the activation energy of sintering via the MSC methodology. The approaches provide reasonable values of the activation energy, whether noise is

present in the data or not. The analytic expressions derived here can also be used to test different kinetic mechanisms and to determine the pre-exponential factor. The origin of the insensitivity of the activation energy obtained from the two analytical expressions is presented next.

One model to clarify the terms appearing in kinetic expressions is transition state theory (TST) [3-5], where the pre-exponential factor arises as a vibration frequency related to converting activated complexes to products. A typical form for the pre-exponential factor in TST is given by:

$$A' = \frac{k_b T}{h} \exp \frac{\Delta S^*}{R} \quad (21)$$

where h is Planck's constant and ΔS^* is the entropy difference between the reactants and activated complexes. Thus, TST theory predicts that the pre-exponential factor depends linearly on temperature.

An alternative representation is to express the kinetics of sintering via the diffusion coefficient and the activity via a modified form of Fick's Law as:

$$J = - \frac{D}{\Omega k_b T} \frac{d\mu}{dx} \quad (22)$$

which is the starting point of the sintering model [27, 31] which underlies the MSC method. The appearance of the inverse dependence on temperature in Eq. 2 thus arises because of the use of the chemical potential, μ , to represent the most general driving force for diffusion and hence sintering. Presumably, if the diffusivity in Eq. 22 were expressed via TST, then the resulting terms which constitute the pre-exponential factor for sintering would not explicitly depend on temperature. Equations 21 and 22 thus illustrate that depending on the starting point and form of the kinetic model, the pre-exponential factor may explicitly depend linearly, inversely, or not at all on temperature.

From a practical viewpoint, however, the dependence of the pre-exponential factor on temperature is often masked, either from measurement error or from other parallel or competing mechanisms, when acquiring kinetic data, and thus the pre-exponential factor is generally taken as a constant. Activation energies are then simply obtained from graphical analysis of rate or rate constant data versus $1/T$. In this work, the role of the factor of $1/T$ in Eq. 5 can thus be handled in different ways, as represented by Eqs. 18 and 19. These two methods, however, lead to similar results, and the underlying reason is that the kinetic behavior is dominated by the exponential function, which dwarfs the weaker dependence on T in the pre-exponential factor.

Conclusions

Two analytic expressions have been derived to determine the activation energy of sintering via the MSC approach, obviating the need for numerical integration. Both expressions lead to accurate values of the activation energy within 1%, even when noise is present in the underlying data. Equation 19 is a very simple mathematical expression that can be used to calculate activation energies of thermally activated systems using the model-free method of the MSC approach and will also produce an MSC curve consistent with what is obtained by numeric integration. Because Eq. 19 can be manipulated analytically in ways that the original integral expression, Eq. 3, cannot, Eq. 19 has the potential to be a useful tool for discriminating between kinetic mechanisms and to determine the pre-exponential factor.

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