

A UNIFIED THEORY FOR THE KINETIC ANALYSIS OF SOLID STATE REACTIONS UNDER ANY THERMAL PATHWAY

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Abstract

The Ozawa concept of generalized time has been used for developing master plots for the different kinetic models describing solid state reactions. These plots can be indistinctly used for analysing isothermal or non-isothermal experimental data. It is demonstrated that it is not possible to discriminate the kinetic model from a single non-isothermal curve without a previous knowledge of the activation energy. However, it has been shown that the $\ln [(d\alpha/dt)/f(\alpha)]$ data taken from a set of DTG curves obtained at different heating rates lie on a single straight line when represented as a function of $1/T$ only if the kinetic model really obeyed by the reaction is considered. Moreover, the true values of E and A are obtained from the slope and the intercept of this straight line.

Keywords: solid state reactions, theory for the kinetic analysis, thermal pathway

Introduction

The kinetic analysis of solid state reactions from experimental thermoanalytical (TA) data recorded under non-isothermal conditions have become very popular [1–10]. The popularity of the non-isothermal methods with regards to the isothermal ones stands on the assumption that the kinetic parameters can be determined from a single non-isothermal experiment although this assumption have been strongly criticised [11–16]. A disagreement between the kinetic parameters obtained for a given solid state reaction from isothermal and non-isothermal methods has been very often reported. This disagreement has been usually interpreted either by assuming that the reaction kinetic depends on the thermal pathway or by considering that non-isothermal methods are not proper for kinetic analysis. The scope of this work is to show that using the concept of ‘reduced time’ introduced by Ozawa [17] it is possible to get generalized ‘master plots’ to be indistinctly used for fitting the experimental data obtained under any thermal pathway.

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Theory

Generalized kinetic equations

The rate of a solid state reaction is expressed by the following general law:

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

that can be rearranged in logarithmic form:

$$\ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln A - \frac{E}{RT} \quad (2)$$

The Ozawa reduced time, θ , is defined as

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (3)$$

that after differentiation becomes

$$\frac{d\theta}{dt} = \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where θ denotes the reaction time taken to attain a particular α at infinite temperature.

Combining Eqs (1) and (3), the following expression is obtained:

$$\frac{d\alpha}{d\theta} = A f(\alpha) \quad (5)$$

or

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{E}{RT}\right) \quad (6)$$

where $d\alpha/d\theta$ corresponds to the generalized reaction rate.

Master plots based on the differential form of the generalized kinetic equation

Using as reference point $\alpha=0.5$, the following equations are easily derived from Eqs (4) and (5)

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{f(\alpha)}{f(0.5)} \quad (7)$$

and

$$\frac{d\alpha/d\theta}{(d\alpha/d\theta)_{\alpha=0.5}} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \frac{\exp(E/RT)}{\exp(E/RT_{0.5})} \quad (8)$$

where $T_{0.5}$ is the reaction temperature at $\alpha=0.5$.

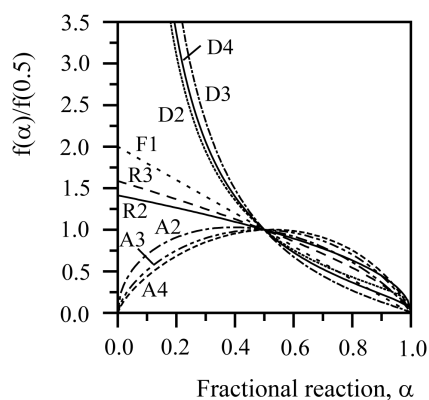


Fig. 1 Theoretical master curves in differential form representing $f(\alpha)/f(0.5)$ as a function of α for the different kinetic models describing solid state reactions

The master plots of $[(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}]$ as a function of α for different kinetic models are shown in Fig. 1. These master plots can be indistinctly used for analysing experimental data obtained under any heating pathway (i.e.; Isothermal, TG, SIA, CRTA, etc.). It must be pointed out that in the case of isothermal data, the experimental master plot can be derived directly from a single isothermal curve of $d\alpha/dt$ vs. α . However, for calculating the reduced-generalized reaction rate at a given α for non-isothermal data, in addition to the experimental data of a single measurement, the value of E for the process should be previously known.

Results

The above analysis allows to conclude that experimental α - T plots obtained under different thermal pathways can be simultaneously analysed by means of the master plot included on Fig. 1. The usefulness of this master plot has been checked by using the experimental data of the isothermal α - T plot, TG and CRTA traces obtained in a previous work for the thermal decomposition of anhydrous ZnCO_3 under high vacuum [18]. It is noteworthy to point out that the temperature of the isothermal run, the heating rate of the DTG curve and the constant reaction rate of the CRTA experiment were selected in such a way that the thermal decomposition of ZnCO_3 occurs in a similar range of temperature on the three experiments, namely between 690 and 740 K. It was reported [18] that the thermal decomposition of ZnCO_3 at temperatures higher than 690 K fitted a F_1 kinetic model with $E=140 \text{ kJ mol}^{-1}$.

Figure 2 compares the theoretical master plots of $f(\alpha)/f(0.5)$ vs. α with the experimental master plots of $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$ as a function of α calculated from the experimental data previously reported for the thermal decomposition of ZnCO_3 . Because the exponential term in Eq. (8) can be neglected for the isothermal kinetic data, the experimental master plot for the isothermal kinetic data was obtained as $(d\alpha/dt)/(d\alpha/dt)_{\alpha=0.5}$ vs. α . The TG and CRTA master plots were calculated from the activation energy $E=140 \text{ kJ mol}^{-1}$ previously obtained from other sources. Figure 2

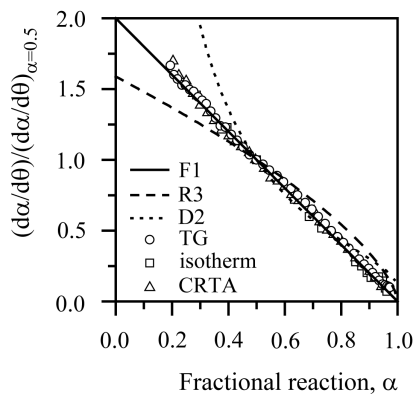


Fig. 2 A comparison of the experimental master plots of $(d\alpha/d\theta)/(d\alpha/d\theta)_{\alpha=0.5}$ vs. α for the thermal decomposition of ZnCO_3 with the theoretical master curves

shows that independently of the heating pathway followed by the reaction, the experimental master plots are in good agreement with the theoretical master plots corresponding to the F_1 mechanism as was previously reported [18].

As a consequence of the above analysis we can conclude that a single TG curve does not permit to discern the kinetic model of a solid state reaction without a previous knowledge of the activation energy. This statement is illustrated in Fig. 3 that shows a curve simulated by assuming a linear heating rate $\beta=10 \text{ K min}^{-1}$, a F_1 kinetic model and the following kinetic parameters: $E=167 \text{ kJ mol}^{-1}$ and $A=9.6 \cdot 10^{-7} \text{ min}^{-1}$. It is clearly shown in this figure that this data can be also fitted by an A_2 kinetic model with $E=76 \text{ kJ mol}^{-1}$ and $A=8.9 \cdot 10^{-2} \text{ min}^{-1}$ and an A_3 kinetic model with the following kinetic parameters: $E=45 \text{ kJ mol}^{-1}$ and $A=1.6 \cdot 10^2 \text{ min}^{-1}$. However, the combined kinetic analysis of a set of TG curves obtained at different heating rates would allow to determine at the

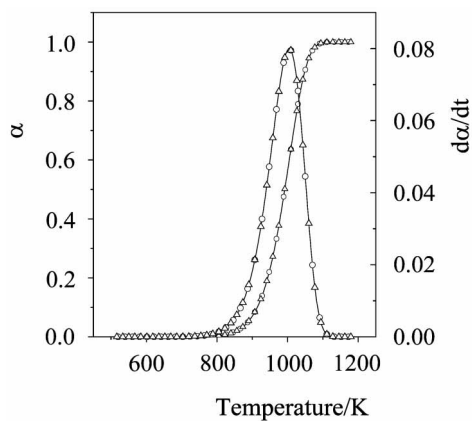


Fig. 3 Simulated TG, DTG curves by assuming linear heating rate conditions ($\beta=10 \text{ K min}^{-1}$), an F_1 kinetic model and the following kinetic parameters: $E=167 \text{ kJ mol}^{-1}$ and $A=9.6 \cdot 10^{-7} \text{ min}^{-1}$ (solid line). Fitting of these curves by $\circ - A_2$ and $\triangle - A_3$ kinetic models

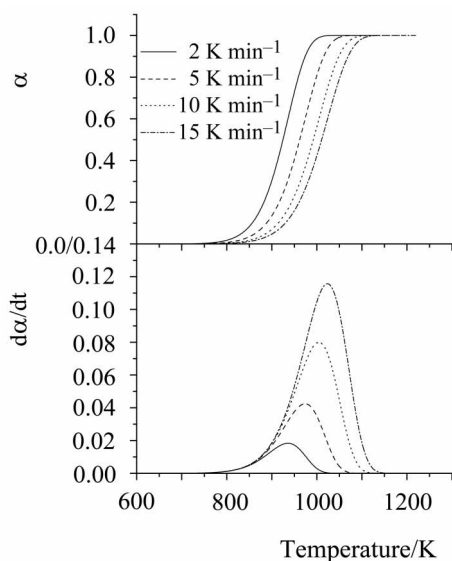


Fig. 4 Simulated curves by assuming different heating rates ($\beta=2, 5, 10$ and 15 K min^{-1} , respectively) and the following kinetic parameters: $E=167 \text{ kJ mol}^{-1}$ and $A=9.6 \cdot 10^7 \text{ min}^{-1}$

time the kinetic model, the activation energy and the preexponential factor of Arrhenius. In order to demonstrate this statement, the set of DTG curves shown in Fig. 4 have been simulated at different heating rates for the same F_1 kinetic model reaction described in Fig. 3 and have been simultaneously analysed by means of Eq. (2) after assuming differ-

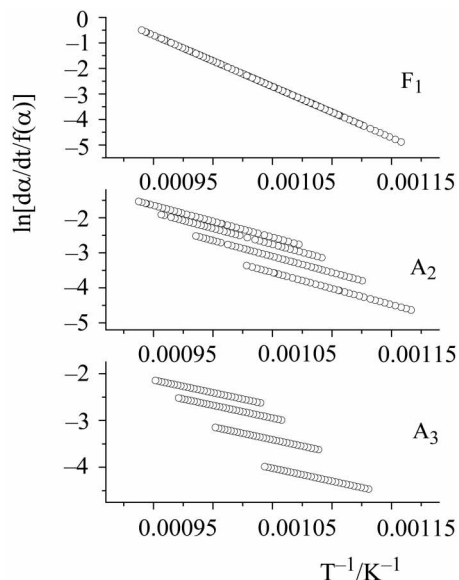


Fig. 5 Analysis of the curves included in Fig. 4 by means of Eq. (2) after assuming the same kinetic models that were overlapping on Fig. 3

ent kinetic models. The results obtained by assuming the kinetic models F_1 , A_2 and A_3 that are shown in Fig. 5 clearly demonstrate that the combined analysis of the results included in Fig. 4 only fit the F_1 kinetic model that was assumed for simulating the set of DTG traces calculated for different heating rates. Moreover, the activation energy and the preexponential factor of Arrhenius determined from the slope and the intercept, respectively, of the single straight line obtained for the F_1 mechanism quite agree with the corresponding values used for simulating the curve included in Fig. 3.

Conclusions

It has been demonstrated that the concept of generalized time introduced by Ozawa allows to generalize the use of the master plots for fitting experimental data independently of the thermal pathway used. On the other hand, it has been demonstrated that the simultaneous plot of the values of $[\ln(d\alpha/dt)]/f(\alpha)$ taken from a set of TG-DTG curves recorded at different heating rates as a function of $1/T$ fit a single straight line only if the real $f(\alpha)$ function fitted by the reaction is considered, leading to the real values of E and A .

References

- 1 N. Regnier and S. Fontaine, *J. Therm. Anal. Cal.*, 64 (2001) 789.
- 2 D. Fatu, *J. Therm. Anal. Cal.*, 65 (2001) 213.
- 3 A. N. Modestov, P. V. Poplaukhin and N. Z. Lyakov, *J. Therm. Anal. Cal.*, 65 (2001) 121.
- 4 L. Baca, J. Plewa, L. Pach and J. Opferman, *J. Therm. Anal. Cal.*, 66 (2001) 803.
- 5 J. Zelic, D. Rusic and R. Krstulovic, *J. Therm. Anal. Cal.*, 67 (2002) 613.
- 6 P. Budrugaec, *J. Therm. Anal. Cal.*, 68 (2002) 131.
- 7 V. M. Bujoreanu, L. Frangu and E. Segal, *J. Therm. Anal. Cal.*, 68 (2002) 787.
- 8 B. Małecka, E. Drozd-Ciesla and A. Malecki, *J. Therm. Anal. Cal.*, 68 (2002) 819.
- 9 L. Abate, I. Blanco, A. Pollicino and A. Recca, *J. Therm. Anal. Cal.*, 70 (2002) 63.
- 10 R. Iordanova, E. Lefterova, I. Uzunov, Y. Dimitriev and D. Klissurski, *J. Therm. Anal. Cal.*, 70 (2002) 393.
- 11 J. M. Criado and J. Morales, *Thermochim. Acta*, 19 (1977) 305.
- 12 J. M. Criado and A. Ortega, *J. Thermal Anal.*, 29 (1984) 1075.
- 13 J. M. Criado, A. Ortega and F. Gotor, *Thermochim. Acta*, 157 (1990) 171.
- 14 J. H. Flynn, *J. Thermal Anal.*, 36 (1990) 1579.
- 15 J. Málek, *Thermochim. Acta*, 200 (1992) 257.
- 16 S. Vyazovkin and C. A. Wight, *Int. Rev. Phys. Chem.*, 17 (1998) 407.
- 17 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 325.
- 18 F. J. Gotor, M. Macías, A. Ortega and J. M. Criado, *Intern. J. Chem. Kinetics*, 30 (1998) 389