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Generalization of the Kissinger equation for several kinetic models

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Abstract

In this work, a generalization of the Kissinger equation was extended to several solid-state kinetic models, and the expressions for the correction term were also deduced from the algebraic equations of the differential ($f(\alpha)$) and integral ($g(\alpha)$) functions.

Keywords: Kinetics; Kissinger method; Mechanism; Non-isothermal

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1. Introduction

The experimental study of solid-state decomposition kinetics by DTA has been performed by several authors [1–6].

The determination of kinetic parameters using the Kissinger method [7,8], probably the most popular in this family of methods, is based on the equation

$$\ln(\beta/T_{\max}^2) = -E/RT_{\max} + \ln(AR/E) \tag{1}$$

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where β is the heating rate (K min^{-1}), T_{max} is the maximum reaction rate temperature (K), E is the activation energy (kJ mol^{-1}), A is the pre-exponential factor (min^{-1}) and $R = 8.3143$ kJ mol^{-1} K^{-1} is the gas constant.

The plot of $\ln(\beta/T^2_{\mathrm{max}})$ against $1/T_{\mathrm{max}}$ should be a straight line with a slope of $-E/R$ and an intercept equal to $\ln(AR/E)$.

However, this method has been criticized, and afterwards modified, for two main reasons.

Firstly, its application is limited to DTA data, assuming that the maximum reaction rate corresponds to the endothermic peak temperature of a DTA curve. Nevertheless, as has been demonstrated by Dollimore et al. [9], the method is generally applicable to any conventional technique based on linearly rising temperature, avoiding error in the T_{max} value.

On the other hand, the Kissinger method assumes that the rate of reaction can be described by an equation of the form

$$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n \tag{2}$$

where α, t and k have the usual meaning and n is the reaction order, which is calculated from the shape index S of the DTA curve according to

$$n = 1.26(S)^{1/2} \tag{3}$$

Eq. (3) has been proposed by Kissinger considering that $E/RT = \infty$ and neglecting the influence of the peak width on the S value.

Nevertheless, several authors [10,11] have pointed out that Eq. (2) has no general validity for heterogeneous solid-state reactions. In fact, this equation can have theoretical significance only in those cases where the value of n is 0, 1/2, 2/3, or 1.

Thus, if it is desired to study the kinetics of solid thermal decomposition reactions by the Kissinger method, under dynamic temperature conditions using a constant heating rate, it is necessary to derive new expressions for Eq. (1), taking into account the different types of rate controlling heterogeneous processes.

In the present work, the generalization of the Kissinger equation is extended to different kinetic models of the type discussed by Brown et al. [12] using differential ($f(\alpha)$) and integral ($g(\alpha)$) functions.

2. Theory

In this sense, the first attempt has been outlined by Elder [13,14]. This author considers that, if the temperature of the sample is increased at a constant rate $\beta = \mathrm{d}T/\mathrm{d}t$, the rate of a thermally induced solid reaction can be written

$$\mathrm{d}\alpha/\mathrm{d}T = \frac{A_m T^m}{\beta}\exp(-E/RT)f(\alpha) \tag{4}$$

where the term $A_m T^m$ ($m = \frac{1}{2}$ or 1), according to the transition state theory, expresses the pre-exponential factor A as a function of temperature [15] and $f(\alpha)$ depends on the type of rate controlling process.

From Eq. (4), and taking into account, as did Kissinger, the condition for the maximum reaction rate on a thermal curve is given by

$$(\mathrm{d}^2\alpha/\mathrm{d}T^2)_{T=T_{\max}} = 0 \tag{5}$$

Elder derived the following generalized Kissinger equation

$$\ln\left(\frac{\beta}{T_{\max}^{m+2}}\right) = -E/RT_{\max} + \ln\left[\frac{AR}{E}\,\phi_m(\alpha_{\max})\right] \tag{6}$$

with a correction term $\phi_m(\alpha_{\max})$, which is a function of the reaction mechanism, given by the equation

$$\phi_m(\alpha_{\max}) = \frac{-f'(\alpha_{\max})}{1 + mRT_{\max}/E} \tag{7}$$

where $\alpha_{\max}$ is the fractional extent of reaction value corresponding to the maximum rate temperature $T_{\max}$.

However, the application of differential or integral methods in the non-isothermal kinetics of solid-state reactions usually assumes, according to the Arrhenius theory, the temperature independence of the pre-exponential factor A. Thus, Eqs. (6) and (7), for $m = 0$, can be simplified to

$$\ln(\beta/T_{\max}^2) = -E/RT_{\max} + \ln\left[\frac{AR}{E}\,\phi_0(\alpha_{\max})\right] \tag{8}$$

and

$$\phi_0(\alpha_{\max}) = -f'(\alpha_{\max}) \tag{9}$$

Table 1
Solid-state kinetic models used for the generalization of the Kissinger equation

Model	Symbol	$f(\alpha)$	$g(\alpha)$
Avrami–Erofeev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofeev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami–Erofeev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout–Tompkins	B1	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
Mampel power law	P1	$n\alpha^{1-1/n}$	$\alpha^{1/n}$
Exponential law	E1	α	$\ln\alpha$
Two-dimensional phase boundary	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Three-dimensional phase boundary	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
One-dimensional diffusion	D1	$(1/2)\alpha$	α^2
Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional diffusion (Jander equation)	D3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{-1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounshtein equation)	D4	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
First order	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Second order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
Third order	F3	$(1/2)(1-\alpha)^3$	$(1-\alpha)^{-2}$

Table 2
Expressions for the correction term derived from $f(\alpha)$ and $g(\alpha)$ functions summarized in Table 1

Mechanism	$\phi_0(\alpha_{\max})$	$W(g(\alpha_{\max}))$
A2	$2[-\ln(1-\alpha_{\max})]^{1/2}-[-\ln(1-\alpha_{\max})]^{-1/2}$	$2g(\alpha_{\max})-g(\alpha_{\max})^{-1}$
A3	$3[-\ln(1-\alpha_{\max})]^{2/3}-2[-\ln(1-\alpha_{\max})]^{-1/3}$	$3g(\alpha_{\max})-2g(\alpha_{\max})^{-1}$
A4	$4[-\ln(1-\alpha_{\max})]^{3/4}-3[-\ln(1-\alpha_{\max})]^{-1/4}$	$4g(\alpha_{\max})-3g(\alpha_{\max})^{-1}$
B1	$2\alpha_{\max}-1$	$(e^{g(\alpha_{\max})}-1)/(e^{g(\alpha_{\max})}+1)$
P1	$(1-n)\alpha_{\max}^{-1/n}$	$(1-n)g(\alpha_{\max})^{-1/n}$
E1	-1	-1
R2	$(1-\alpha_{\max})^{-1/2}$	$[1-g(\alpha_{\max})]^{-1}$
R3	$2(1-\alpha_{\max})^{-1/3}$	$2[1-g(\alpha_{\max})]^{-1}$
D1	$(1/2)\alpha_{\max}^{-2}$	$(1/2)g(\alpha_{\max})^{-1}$
D2	$(1-\alpha_{\max})^{-1}[-\ln(1-\alpha_{\max})]^{-2}$	–
D3	$\dfrac{(1-\alpha_{\max})^{-1/3}-1/2}{[1-(1-\alpha_{\max})^{1/3}]^2}$	$\dfrac{1+2g(\alpha_{\max})^{1/2}[1-g(\alpha_{\max})^{1/2}]^{-1}}{2g(\alpha_{\max})}$
D4	$\dfrac{(1/2)(1-\alpha_{\max})^{-4/3}}{[(1-\alpha_{\max})^{-1/3}-1]^2}$	–
F1	1	1
F2	$2(1-\alpha_{\max})$	$2g(\alpha_{\max})^{-1}$
F3	$(3/2)(1-\alpha_{\max})^2$	$(3/2)g(\alpha_{\max})^{-1}$

The plot of the left hand side of Eq. (8) vs. $1/T_{\max}$ should be a straight line from whose slope the activation energy can be calculated.

As can easily be seen by comparing Eq. (8) with Eq. (1), the correction term $\phi_0(\alpha_{\max})$ affects the intercept value, which is constant only for first order processes because, in this particular case, $\phi_0(\alpha_{\max}) = 1$.

Nevertheless, several authors [16,18] have shown that, for the remaining kinetic models, the error in the activation energy directly calculated from the slope of a $\ln(\beta/T_{\max}^2)$ vs. $1/T_{\max}$ plot does not exceed 5%. Thus, it seems reasonable to assume that the pre-exponential factor A must be the kinetic parameter that reflects most significantly the effect induced by the correction term.

From Eq. (9), using the $f(\alpha)$ functions for the solid-state kinetic models summarized in Table 1, we have derived the expressions for $\phi_0(\alpha_{\max})$ presented in Table 2.

On the other hand, as is well known, the non-isothermal kinetics of solid decomposition reactions can be studied by methods based on the integral kinetic equation, which can be written

$$\int_0^{\alpha} \mathrm{d}\alpha/f(\alpha) = (A/\beta)\int_{T_0}^{T} \exp(-E/RT)\,\mathrm{d}T \tag{10}$$

or, in short form

$$g(\alpha) = S(T) \tag{11}$$

where the temperature-dependent part of Eq. (10), $S(T)$, cannot be solved analytically.

Taking as a reference the method developed by Wimmers [19] to calculate TPR patterns using reduction kinetic models and to analyze the influence of the heating rate on the TPR peak maximum, we will afterwards derive the expressions for the correction term in function of the $g(\alpha)$ equation for the several reaction mechanisms listed in Table 1, using Eq. (11), proposed by Wimmers, as a starting point.

For our purposes we selected as an example the Jander three-dimensional diffusion model.

Inserting in Eq. (11) the $g(\alpha)$ expression for a D3 mechanism, we obtain

$$[1-(1-\alpha)^{1/3}]^2 = S(T) \tag{12}$$

Eq. (12) can be written

$$\alpha = 1-[1-S(T)^{1/2}]^3 \tag{13}$$

By differentiating with respect to T, Eq. (13) becomes

$$\mathrm{d}\alpha/\mathrm{d}T = (3/2)[1-S(T)^{1/2}]^2 S(T)^{-1/2}\,\mathrm{d}S(T)/\mathrm{d}T \tag{14}$$

From Eq. (11), if T_0 is much smaller than T, it can be established that

$$\mathrm{d}S(T)/\mathrm{d}T = (A/\beta)\exp(-E/RT) \tag{15}$$

By substituting Eq. (15) into Eq. (14), one obtains:

$$\mathrm{d}\alpha/\mathrm{d}T = (3/2)[1-S(T)^{1/2}]^2 S(T)^{-1/2}(A/\beta)\exp(-E/RT) \tag{16}$$

Taking into account the condition for the maximum reaction rate given by Eq. (5), we can write

$$\begin{aligned}&(3/2)[1-S(T_{\max})^{1/2}]S(T_{\max})^{-1/2}(\mathrm{d}S(T)/\mathrm{d}T)_{T=T_{\max}}\{E/RT_{\max}^2(1-S(T_{\max})^{1/2})\\ &\quad -[(1/2)(1-S(T_{\max})^{1/2})S(T_{\max})^{-1}+S(T_{\max})^{-1/2}](\mathrm{d}S(T)/\mathrm{d}T)_{T=T_{\max}}\}=0\end{aligned} \tag{17}$$

and, combining Eq. (17) with Eq. (15), we obtain after collecting terms

$$\begin{aligned}E/RT_{\max}^2(1-S(T_{\max})^{1/2}) &= (A/\beta)\exp[-(E/RT_{\max})]\\ &\quad\times[(1/2)(1-S(T_{\max})^{1/2})S(T_{\max})^{-1}+S(T_{\max})^{-1/2}]\end{aligned} \tag{18}$$

Since, according to Eq. (11), $S(T_{\max}) = g(\alpha_{\max})$, we can write Eq. (18), after rearranging, in the form

$$\beta/T_{\max}^2 = \exp(-E/RT_{\max})(AR/E)\left[(1/2)g(\alpha_{\max}) + \frac{(1-g(\alpha_{\max})^{1/2})^{-1}}{g(\alpha_{\max})^{1/2}}\right] \tag{19}$$

Taking logarithms, one obtains after collecting terms

$$\ln(\beta/T_{\max}^2) = -E/RT_{\max} + \ln\left[AR/E\,\frac{1+2g(\alpha_{\max})^{1/2}(1-g(\alpha_{\max})^{1/2})^{-1}}{2g(\alpha_{\max})}\right] \tag{20}$$

As can be seen from a comparison of Eqs. (1) and (20), the intercept of the $\ln(\beta/T_{\max}^2)$ vs. $1/T_{\max}$ plot is again affected by a correction term which gives account of the reaction mechanism (D3, in this particular case) through the $g(\alpha)$ kinetic equation.

In a general way, we can write

$$\ln(\beta/T_{\max}^2) = -E/RT_{\max} + \ln\left[\frac{AR}{E} W(g(\alpha_{\max}))\right] \tag{21}$$

The correction term $W(g(\alpha_{\max}))$ for the remaining kinetic models considered in this work, which have been deduced following a similar procedure, are presented in Table 2.

For the D2 and D4 mechanisms, the derivation of a relationship of the type $\alpha = f(S(T))$ is not immediate, thus no deduction of $W(g(\alpha_{\max}))$ for these cases has been made.

It must also be pointed out that the generalized Kissinger equation for the E1 mechanism has no physical meaning because $\phi_0(\alpha_{\max}) = W(g(\alpha_{\max})) = -1$.

Obviously, and it is easy to verify, the expression for the Kissinger equation, taking into account the reaction mechanism, must be the same independently of the method used for its deduction.

For example, we will again consider the D3 mechanism. The expression for the correction term deduced by using the Elder method is (see Table 2)

$$\phi_0(\alpha_{\max}) = \frac{(1-\alpha_{\max})^{-1/3} - 1/2}{[1-(1-\alpha_{\max})^{1/3}]^2} \tag{22}$$

and from the Wimmers method (see Eq. (20))

$$W(g(\alpha_{\max})) = \frac{1 + 2g(\alpha_{\max})^{1/2}[1 - g(\alpha_{\max})^{1/2}]^{-1}}{2g(\alpha_{\max})} \tag{23}$$

By substituting $g(\alpha_{\max}) = [1-(1-\alpha_{\max})^{1/3}]^2$ into Eq. (23), and after collecting terms, we obtain

$$\begin{aligned} W(g(\alpha_{\max})) &= \frac{1 + 2[1-(1-\alpha_{\max})^{1/3}](1-\alpha_{\max})^{-1/3}}{2[1-(1-\alpha_{\max})^{1/3}]^2} \\ &= \frac{(1-\alpha_{\max})^{-1/3} - 1/2}{[1-(1-\alpha_{\max})^{1/3}]^2} \end{aligned} \tag{24}$$

which is identical to Eq. (22).

3. Conclusions

The classic Kissinger equation proposed for the determination of kinetic parameters from DTA curves and developed for reactions of order n can be generalized to different rate controlling heterogeneous processes, including the Avrami–Erofeev, Prout–Tompkins, Mampel, exponential law, phase boundary movement, diffusional and nth order models.

The generalized Kissinger equation would allow the simultaneous determination of both the reaction mechanism and the kinetic parameters from several rising temperature experiments at constant heating rate.

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References

[1] H.L. Friedman, in H.G. McAdie (Ed.), Proceedings of the Third Toronto Symposium on Thermal Analysis, Chemical Institute of Canada, Toronto, 1969, p. 127.
[2] J. Šesták and G. Berggren, Svazek, 64 (1970) 695.
[3] C.B. Murphy, Miner. Sci. Eng., 3 (1970) 51.
[4] P. Murray and J. White, Trans. Br. Ceram. Soc., 54 (1955) 205.
[5] J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
[6] J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam, 1984.
[7] H.E. Kissinger, J. Res. Natl. Bur. Stand., 57 (1956) 217.
[8] H.E. Kissinger, Anal. Chem., 29(11) (1957) 1702.
[9] D. Dollimore, C. Guler and G.R. Heal, Thermochim. Acta, 54 (1982) 187.
[10] B.N.N. Achar, G.W. Brindley and J.H. Sharp, Proc. Int. Clay Conf. Jerusalem, Vol. 1, 1966, p. 67.
[11] J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
[12] M.E. Brown, D. Dollimore and A.K. Galwey, in C.F.H. Tippers (Ed.), Comprehensive Chemical Kinetics, Elsevier, Amsterdam, 1980, p. 340.
[13] J.P. Elder, in P.S. Gill and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 5, Plenum Press, New York, 1984, p. 269.
[14] J.P. Elder, J. Therm. Anal., 30 (1985) 655.
[15] D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 54 (1982) 181.
[16] J.M. Criado and A. Ortega, J. Non-Cryst. Solids, 87 (1986) 302.
[17] S. Akhouayri. Thesis, University of Provence, Marseille, 1989, p. 59.
[18] J. Málek, J. Šesták, F. Rouquérol, J. Rouquérol, J.M. Criado and A. Ortega, J. Therm. Anal., 38 (1992) 71.
[19] O.J. Wimmers, Thermochim. Acta, 95 (1985) 67.