APPlicabilIty of the Kissinger EqUation in thermal analysis
revisited

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For the most common kinetic models used in heterogeneous reactions, the dependencies on \( x_m = E/RT_m \) (\( E \) is the activation energy, \( T_m \) is the temperature corresponding to maximum process rate, \( R \) is the gas constant) on the relative errors (\( \epsilon \% \)) in the determination of the activation energy from the slope of the Kissinger straight line \( \ln(\beta / T_m^2) \) vs. \( 1/T_m \) (\( \beta \) is the heating rate) are evaluated. It is pointed out that, for \( x_m=10.7 \) and all kinetic models, \( |\epsilon\%| \leq 5\% \). Some possible cases exhibiting high values of \( |\epsilon\%| \), which can be higher than 10\%, are put in evidence and discussed.

**Keywords:** Kissinger equation, non-isothermal kinetics

Introduction

According to Kissinger [1], for an Arrhenius dependence of the rate constant on temperature, and the ‘reaction order model’ of the conversion function, one obtains:

\[
\ln \frac{\beta}{T_m^2} = \ln \frac{AR}{E} + \ln[n(1 - \alpha_m)^{n+1}] - \frac{E}{RT_m} \tag{1}
\]

where \( E \) is the activation energy, \( A \) is the pre-exponential factor, \( \beta \) is the heating rate, \( n \) is the reaction order, \( \alpha \) is the conversion degree, \( T \) is the temperature, \( R \) is the gas constant; index \( m \) is used for the maximum of the reaction rate.

As \( 1-\alpha_m \) is a constant for a given value of \( n \), a value for \( E \) may be obtained from the slope of the plot \( \ln(\beta / T_m^2) \) vs. \( 1/T_m \) for a series of experiments at different heating rates.

The fact that the \( T_m \) values for various heating rates can be precisely evaluated from non-isothermal data (DTG, DTA or DSC curves) conferred to the Kissinger method to evaluate the kinetic parameters a high popularity ([2–14] refer to very recent published papers in which this method was used).

Since its appearance, the problem of applicability of Kissinger method for other kinetic models as An (Avrami–Erofeev or JMAEK) and Dn (diffusion models) arisen. Elder [15] has generalized the Kissinger treatment to make applicable to the full range of kinetic models. The corresponding equation is:

\[
\ln \frac{\beta}{T_m^2} = \ln \frac{AR}{E} + \ln \delta_m - \frac{E}{RT_m} \tag{2}
\]

where

\[
\delta_m = - \frac{df(\alpha_m)}{d\alpha_m} \tag{3}
\]

\( f(\alpha) \) being the differential function of conversion.

\( \ln \delta_m \) is a correction term, which depends on the kinetic model. The influence of this term on the values of the activation parameters (\( E \) and \( A \)) was investigated [15] for simulated data corresponding to \( E=220 \text{ kJ mol}^{-1} \) and \( A=10^{15} \text{ min}^{-1} \), the kinetic models R2, R3, F1, F2, A2, A3, D2, D3 and D4 (the analytical forms of \( f(\alpha) \) and \( g(\alpha) = \int_0^\alpha \frac{do}{f(\alpha)} \) corresponding to these kinetic models has been published in many papers (for example [16]) and heating rates comprised between 1 and 100 K min\(^{-1}\). It turns out that when using both Eqs (1) and (2), the values of \( E \) agree with that used for simulation. On the other hand, it has been proved that the use of relation (2) leads to values of \( A \) in agreement with that used at the simulation, while neglecting the correction term \( \ln \delta_m \) leads to values of \( A \) which depend on the kinetic model (the highest differences were obtained for the models D3 and D4). We note that for the examples considered by Elder [15] the values of \( x_m = E/RT_m \) are comprised in the range 32.3\( \leq x_m \leq 39.8 \). Elder’s analysis for these particular cases does not justify the conclusion general accepted according to which the values of \( E \) obtained from the

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slopes of the straight lines ln(β / T_m^2) vs. 1/T_m are not sensitive to the correct choice of the kinetic model.

Nevertheless several authors [17, 18] have shown that, for some kinetic models, the errors in the activation energy directly calculated from the slope of a ln(β / T_m^2) vs. 1/T_m plot does not exceed 5%.

Llopiz et al. [19] calculated ln(δ_m) values vs. g(α_m) and considered that this correction term should be used for the correct evaluation of A from the intercept of the straight line ln(β / T_m^2) vs. 1/T_m.

The dependence of ln(δ_m) on α_m that depends on the kinetic model and x_m [20] shows that principally E determined from the slope of the straight line ln(β / T_m^2) vs. 1/T_m differs from the value determined taking into account the mentioned correction term.

In this paper we aim to determine for each kinetic model the value of x_m corresponding to a given relative error in the activation energy obtained from the slope of the straight line ln(β / T_m^2) vs. 1/T_m.

### Kissinger equation and the error of E evaluation from the slope of the straight line ln(β / T_m^2) vs. 1/T_m

Relation (2) results directly from the reaction rate equation:

$$\beta \frac{d\alpha}{dT} = Af(\alpha) \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (4)

and the condition of maximum reaction rate:

$$\frac{d^2\alpha}{dT^2} = 0 \text{ for } T=T_m$$  \hspace{1cm} (5)

It turns out that:

$$E = -R \left[\ln\left(\frac{\beta}{T_m^2}\right) + \frac{1}{T_m} \right] - \frac{d\ln(\delta_m)}{dx_m}$$  \hspace{1cm} (6)

It follows that the activation energy determined from the slope of the straight line ln(β / T_m^2) vs. 1/T_m should be corrected with the factor 1/[1–(dln(δ_m)/dx_m)]. But dln(δ_m)/dx_m depends on x_m that depends on T_m. We are going to show that in practical cases where ΔT_m does not exceed 150 K, dln(δ_m)/dx_m exhibits a rather small change round an average value. This is the reason for:

$$E = -R \left[\ln\left(\frac{\beta}{T_m^2}\right) + \frac{1}{T_m} \right] - \frac{\text{dln}(\delta_m)}{\text{dx}_m}$$  \hspace{1cm} (7)

On the other hand, the evaluation of the activation energy using Kissinger method is generally performed considering that

$$E_{\text{approx.}} = -R \frac{\left(\ln\left(\frac{\beta}{T_m^2}\right) + \frac{1}{T_m} \right)}{d\ln(\delta_m)/dx_m}$$

Thus the approximate value of E is given by:

$$E_{\text{approx.}} = -R \frac{\left(\ln\left(\frac{\beta}{T_m^2}\right) + \frac{1}{T_m} \right)}{d\ln(\delta_m)/dx_m}$$  \hspace{1cm} (8)

The relative error of E_{approx.} with respect to the true one is given by:

$$e% = \frac{E_{\text{approx.}} - E}{E} \times 100 = -100 \frac{\text{dln}(\delta_m)}{\text{dx}_m}$$  \hspace{1cm} (9)

The aim of this paper is the evaluation of the dependence e% vs. x_m for the most kinetic models used in heterogeneous reactions.

### Evaluation of δ_m and e%

The integral form of the reaction rate equation (Eq. (4)) for x=x_m is:

$$g(\alpha_m) = \frac{AE}{\beta R} p(x_m) = \frac{AE}{\beta R} e^{-x_m} - h(x_m)$$  \hspace{1cm} (10)

where p(x) is the temperature integral and

$$h(x_m) = 1 - x_m^2 e^{-x_m}.$$  \hspace{1cm}

From relations (2) and (10) we get:

$$\delta_m g(\alpha_m) = 1 - h(x_m)$$  \hspace{1cm} (11)

Relation (11) is valid for all the kinetic models describing the non-isothermal heterogeneous changes (Table 1) except D1 model for which α_m=1 and δ_m=0.5. This is the general form of the relation derived by Gao et al. [20] who kept only the first two terms from the asymptotic expansion of p(x) (for this approximation: h(x_m)=2/x_m).

In the following, we will use for p(x) the 4th rational expression of Senum and Yang [21]:

$$p(x) = \frac{e^{-x}}{x} \left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right)$$  \hspace{1cm} (12)

which exhibits a relative error in p(x) evaluation lower than 0.6% for x≥1.

The expressions of α_m and δ_m listed in Table 1 were obtained using relation (11). These expressions were used for evaluations of the dependencies δ_m vs.