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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 (e%) in the determination of the activation energy from the slope of the Kissinger straight line $\ln(\beta/T_m^2)$ *vs.* $1/T_m$ (β is the heating rate) are evaluated. It is pointed out that, for $x_m \geq 10.7$ and all kinetic models, $|e\%| \leq 5\%$. Some possible cases exhibiting high values of $|e\%|$, 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:

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

where E is the activation energy, A is the pre-exponential factor, β is the heating rate, n is the reaction order, α 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:

$$\ln\frac{\beta}{T_m^2}=\ln\frac{AR}{E}+\ln\delta_m-\frac{E}{RT_m} \qquad (2)$$

where

$$\delta_m=-\frac{df(\alpha_m)}{d\alpha_m} \qquad (3)$$

$f(\alpha)$ 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 kJ mol^{-1} and A=10^{15} min^{-1}, the kinetic models R2, R3, F1, F2, A2, A3, D2, D3 and D4 (the analytical forms of $f(\alpha)$ and $g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ 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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slope of the straight lines $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$ 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 $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$ plot does not exceed 5%.

Llopiz *et al.* [19] calculated $\ln\delta_{\mathrm{m}}$ values *vs.* $g(\alpha_{\mathrm{m}})$ and considered that this correction term should be used for the correct evaluation of A from the intercept of the straight line $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$.

The dependence of $\ln\delta_{\mathrm{m}}$ on α_{m} that depends on the kinetic model and x_{m} [20] shows that principially E determined from the slope of the straight line $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$ 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 $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$.

Kissinger equation and the error of *E* evaluation from the slope of the straight line $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$

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

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{4}$$

and the condition of maximum reaction rate:

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2} = 0 \text{ for } T=T_{\mathrm{m}} \tag{5}$$

It turns out that:

$$E = -R\frac{\mathrm{d}\left(\ln\frac{\beta}{T_{\mathrm{m}}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)}\frac{1}{1-\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}x_{\mathrm{m}}}} \tag{6}$$

It follows that the activation energy determined from the slope of the straight line $\ln(\beta / T_{\mathrm{m}}^2)$ *vs.* $1/T_{\mathrm{m}}$ should be corrected with the factor $1/[1-(\mathrm{d}\ln\delta_{\mathrm{m}}/\mathrm{d}x_{\mathrm{m}})]$. But $\mathrm{d}\ln\delta_{\mathrm{m}}/\mathrm{d}x_{\mathrm{m}}$ 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, $\mathrm{d}\ln\delta_{\mathrm{m}}/\mathrm{d}x_{\mathrm{m}}$ exhibits a rather small change round an average value. This is the reason for:

$$E = -R\frac{\mathrm{d}\left(\ln\frac{\beta}{T_{\mathrm{m}}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)}\frac{1}{\overline{1-\left(\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}x_{\mathrm{m}}}\right)}} \tag{7}$$

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

$$\frac{1}{\overline{1-\left(\frac{\mathrm{d}\ln\delta_{m}}{\mathrm{d}x_{m}}\right)}}\approx 1$$

Thus the approximate value of E is given by:

$$E_{\mathrm{approx.}} = -R\frac{\mathrm{d}\left(\ln\frac{\beta}{T_{\mathrm{m}}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)} \tag{8}$$

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

$$e\% = \frac{E_{\mathrm{approx.}}-E}{E}\cdot 100 = -100\overline{\left(\frac{\mathrm{d}\ln\delta_{\mathrm{m}}}{\mathrm{d}x_{\mathrm{m}}}\right)} \tag{9}$$

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 $x=x_{\mathrm{m}}$ is:

$$g(\alpha_{\mathrm{m}}) = \frac{AE}{\beta R}p(x_{\mathrm{m}}) \equiv \frac{AE}{\beta R}\frac{e^{-x_{\mathrm{m}}}}{x_{\mathrm{m}}^2}[1-h(x_{\mathrm{m}})] \tag{10}$$

where $p(x)$ is the temperature integral and $h(x_{\mathrm{m}}) = 1 - x_{\mathrm{m}}^2 e^{x_{\mathrm{m}}}$.

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

$$\delta_{\mathrm{m}}g(\alpha_{\mathrm{m}})=1-h(x_{\mathrm{m}}) \tag{11}$$

Relation (11) is valid for all the kinetic models describing the non-isothermal heterogeneous changes (Table 1) except D1 model for which $\alpha_{\mathrm{m}}=1$ and $\delta_{\mathrm{m}}=0.5$. 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: $h(x_{\mathrm{m}})\approx 2/x_{\mathrm{m}}$).

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

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

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

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.*

Table 1 Expressions for α_m and δ_m corresponding to the kinetic models from Table 1

Kinetic model	α_m	δ_m
F1	$1-\exp[h(x_m)-1]$	1
Fn $n\neq1$	$1-\left[\frac{1+(n-1)h(x_m)}{n}\right]^{\frac{1}{n-1}}$	$1+(n-1)h(x_m)$
An	$1-\exp\left[\frac{h(x_m)}{n}-1\right]$	$n\left[1-\frac{h(x_m)}{n}\right]^{1-\frac{1}{n}}-(n-1)\left[1-\frac{h(x_m)}{n}\right]^{-\frac{1}{n}}$
D2	from the numerical solution of equation: $\frac{\alpha_m+(1-\alpha_m)\ln(1-\alpha_m)}{(1-\alpha_m)[-\ln(1-\alpha_m)]^2}=1-h(x_m)$	$\frac{1}{(1-\alpha_m)[-\ln(1-\alpha_m)]^2}$
D3	$1-\left[\frac{3}{2}-h(x_m)\right]^{-3}$	$\frac{1-h(x_m)}{\{1-[3/2-h(x_m)]^{-1}\}^2}$
D4	from the numerical solution of equation: $\frac{1-2\alpha_m/3-(1-\alpha_m)^{2/3}}{(1-\alpha_m)^{2/3}[1-(1-\alpha_m)^{1/3}]^2}=2-2h(x_m)$	$\frac{(1-\alpha_m)^{-4/3}}{2[(1-\alpha_m)^{-1/3}-1]^2}$

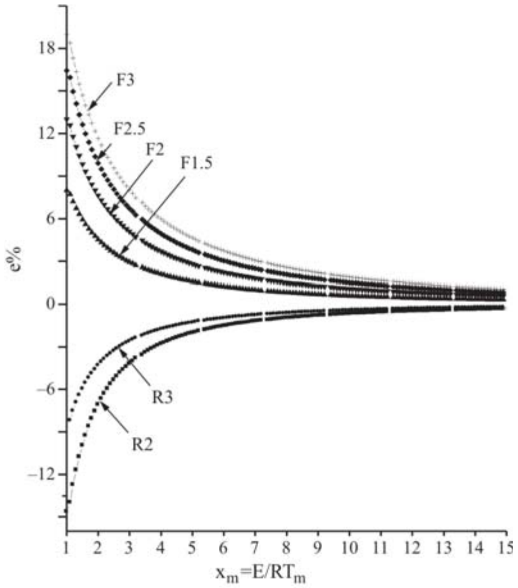

Fig. 1 Dependencies $e\%$ *vs.* x_m for the kinetic models Fn (n=1/2, 2/3, 1.5, 2, 2.5, 3)

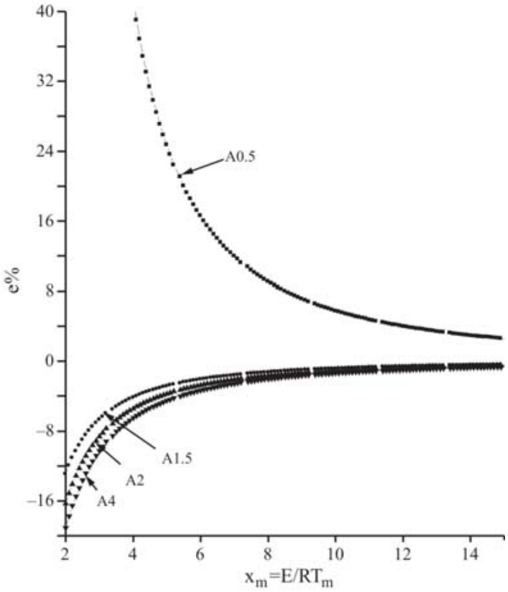

Fig. 2 Dependencies $e\%$ *vs.* x_m for the kinetic models An (n=0.5, 1.5, 2, 4). For the figure clarity, the curve $e\%$ *vs.* x_m for the kinetic model A3, which is between the curves corresponding to the kinetic models A2.5 and A3, was not given

x_m corresponding to the following kinetic models: R2, R3, F1.5, F2, F2.5, F3, A0.5, A1.5, A2, A2.5, A3, A4, D2, D3 and D4. By numerical differentiating of these curves, the dependencies $e\%$ *vs.* x_m were obtained. As results from Figs 1–3, for all kinetic models, $|e\%|$ decreases asymptotically with x_m to $e\%=0$ (the value of $e\%$ for F1 kinetic model).

Table 2 lists the minimum values of x_m for values of the relative error of E obtained from the slope of the straight line $\ln(\beta/T_m^2)$ *vs.* $1/T_m$ (Relation (9)). For $x_m\geq20$ (most frequent cases) for all kinetic models except A0.5, $|e\%|<1\%$; for the model A0.5 $|e\%|=1.34\%$. For a given value of $e\%$ the highest values of $(x_m)_{min}$ correspond to the kinetic models A0.5, D2, D3 and D4.

Possible cases with $|e\%|>5\%$

Case 1

Let us consider the case with E determined from the slope of the straight line $\ln(\beta/T_m^2)$ *vs.* $1/T_m$ equal with 20.0 kJ mol^{-1}, and T_m corresponding to various heating rates in the range 343.6–429.6 K ($5.6\leq x_m\leq7.0$). The values of $e\%$ evaluated using the values of $d\ln\delta_m/dx_m$ are shown in Fig. 4. The $e\%$ values corresponding to the average value of $d\ln\delta_m/dx_m$ exhibit relative standard deviations, which do not ex-

Table 2 Minimum values of x_m for various values of the relative error of E evaluation from the slope of the straight line $\ln(\beta / T_m^2)$ *vs.* $1/T_m$

Kinetic model	|e%|									
	1	2	3	4	5	6	7	8	9	10
R2	7.86	5.04	3.82	3.10	2.65	2.31	2.04	1.81	1.64	1.50
R3	5.90	3.63	2.67	2.16	1.75	1.50	1.31	1.12	<1	<1
F1.5	6.87	4.13	2.95	2.24	1.81	1.47	1.24	1.00	<1	<1
F2	10.46	6.50	4.75	3.75	3.04	2.56	2.19	1.88	1.69	1.45
F2.5	13.11	8.23	6.05	4.80	3.95	3.38	2.87	2.52	2.23	1.97
F3	15.31	9.58	7.11	5.65	4.65	3.98	3.45	3.00	2.67	2.39
A0.5	24.03	16.9	13.88	11.93	10.70	9.73	9.07	8.51	8.01	7.62
A1.5	9.14	6.19	4.84	4.13	3.62	3.22	2.94	2.70	2.51	2.35
A2	10.74	7.26	5.72	4.84	4.25	3.77	3.43	3.14	2.93	2.73
A2.5	11.38	7.70	6.06	5.13	4.47	3.97	3.62	3.34	3.08	2.89
A3	11.70	7.94	6.24	5.24	4.59	4.11	3.74	3.44	3.17	2.97
A4	12.02	8.18	6.40	5.39	4.73	4.20	3.83	3.51	3.26	3.06
D2	11.90	9.06	7.84	6.97	6.45	6.05	5.75	5.45	5.25	5.06
D3	18.98	13.63	11.29	9.84	8.96	8.24	7.69	7.24	6.90	6.56
D4	14.55	10.85	9.14	8.06	7.43	6.93	6.48	6.21	5.09	5.64

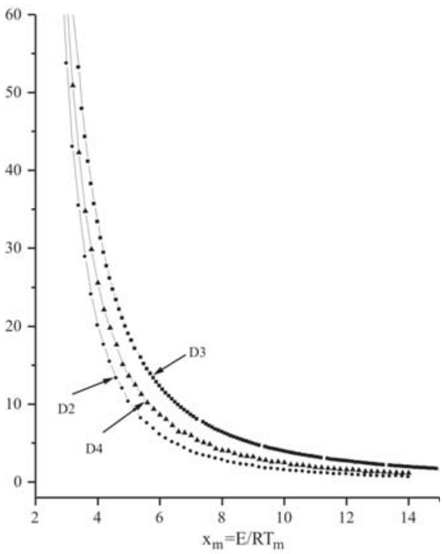

Fig. 3 Dependencies $e\%$ *vs.* x_m for the kinetic models Dn (n=2, 3, 4)

ceed 15%. One notes that: $|e\%|>5\%$ for the diffusion and A0.5 models; $|e\%|>10\%$ only for A0.5 and D3 kinetic models. Using relation (7) for these two models, the following correct values of the activation energy are obtained: E=17.4±0.2 kJ mol^{-1} for A0.5; E=18.0±0.3 kJ mol^{-1} for D3.

Table 3 The characteristic parameters of the simulated non-isothermal data

β/K min^{-1}	T_m/K	x_m	$\ln\delta_m$	$d\ln\delta_m/dx_m$
2	665.15	7.344	2.70277	–0.0770
5	732.65	6.567	2.77096	–0.1012
10	790.65	6.085	2.82345	–0.1185
15	828.65	5.806	2.85851	–0.1323
20	857.15	5.613	2.88518	–0.1427

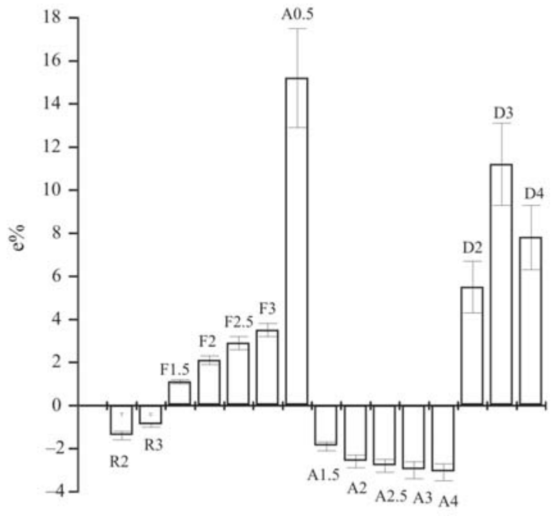

Fig. 4 The values of $e\%$ for E determined from the slope of the straight line $\ln(\beta / T_m^2)$ *vs.* $1/T_m$ equal with 20.0 kJ mol^{-1} and $5.6\le x_m\le 7.0$. Each error bar corresponds to the considered range of x_m

Case 2. Simulated data for E=40 kJ mol^{-1}, A=2 min^{-1}, the kinetic model D3 and the heating rates 2, 5, 10, 15 and 20 K min^{-1}

The data were simulated using for $p(x)$ the 4th rational approximation of Senum and Yang [21] (relation (12)). Table 3 shows the necessary parameters for calculating E using Kissinger's method. Using these data, the value of E evaluated from the slope of the straight line $\ln(\beta / T_m^2)$ *vs.* $(1/T_m)$ is 44.3±0.2 kJ mol^{-1}, which corresponds to $e\%$=11%. A close value of $e\%$ (10.8±2.0%) is obtained by using relation (9) for the range of x_m corresponding to the analyzed case ($5.613\le x_m\le 7.344$; step of x_m is 0.1). A value of E closed to that used for simulation results by using relation (7) (E=40±0.7 kJ mol^{-1}).

Conclusions

It was shown that the relative error, *e*%, of activation energy evaluation through Kissinger's procedure (from the slope of the straight line $\ln(\beta / T_m^2)$ *vs*. $1/T_m$) depends on the kinetic model of the considered reaction as well as on $x_m=E/RT_m$. For each from the most common kinetic models used in heterogeneous reactions, the minimum values of x_m corresponding to *e*% in the range 1–10% were determined. It was pointed out that for all kinetic models $|e\%|\leq 5\%$ for $x_m\geq 10.7$. For a certain x_m, the highest values of $|e\%|$ were obtained for the kinetic models A0.5, D2, D3 and D4.

The theoretical results were verified and discussed for two cases with $|e\%|\geq 5\%$.

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