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# Evaluation of the solutions of a standard kinetic equation for non-isothermal conditions

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## Abstract

It is shown that the method of solving the temperature integral in a standard kinetic equation for non-isothermal conditions affects the value of the estimated activation energy $E$ and the frequency factor $A$ for the known mechanism of conversion. A compensation dependence is suggested as a control test, as well as a kinetic equation solution derived from Coats–Redfern considerations.

## INTRODUCTION

Most frequently, the standard kinetic equation for non-isothermal conditions, also called the kinetic temperature equation, is presented in the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q} f(\alpha)\, \mathrm{e}^{-E/RT} \qquad \alpha \in \langle 0, 1 \rangle \tag{1}$$

or

$$\ln \frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)} = \ln \frac{A}{q} - \frac{E}{RT} \tag{1'}$$

which after the separation of the variables, may be presented as follows:

$$\int \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{q} \int \mathrm{e}^{-E/RT}\, \mathrm{d}T + C \tag{2}$$

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{q} \int_{T_p}^{T} \mathrm{e}^{-E/RT}\, \mathrm{d}T \tag{3}$$

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The importance of the temperature $T_p$ for homogeneous reactions taking place in the liquid phase is expressed in the form [1]

$$T = T_p + q\tau \qquad \text{when } q > 0 \tag{4}$$

Assuming in eqn. (1) that

$$\alpha = 1 - x \tag{5}$$

and

$$f(\alpha) = (1-\alpha)^n = x^n \qquad n > 0 \tag{6}$$

for $T = T_m$, the pertinence of the following relationships (we omit the proof) may be demonstrated:

$$\left.\begin{aligned} &n(1-\alpha_m)^{n-1} = 1 && \text{when } n \neq 1 \\ &1 - \alpha_m = \mathrm{e}^{-1} && \text{when } n = 1 \end{aligned}\right. \tag{7}$$

as well as

$$\frac{ART_m^2}{qE}\mathrm{e}^{-E/RT_m} = 1 \qquad \text{when } n > 0 \tag{8}$$

In the present considerations, condition (8) must be fulfilled by eqns. (1)–(3), taking into account eqn. (6).

Equations (2) and (3) are expressed as follows:

$$\left.\begin{aligned} &\text{for } n \neq 1 \quad C_1 - \frac{(1-\alpha)^{1-n}}{1-n} \\ &\text{for } n = 1 \quad C_2 - \ln(1-\alpha) \end{aligned}\right\} = G(\alpha) = \frac{A}{q}I(T) \tag{9}$$

$$\left.\begin{aligned} &\text{for } n \neq 1 \quad \frac{1-(1-\alpha)^{1-n}}{1-n} \\ &\text{for } n = 1 \quad -\ln(1-\alpha) \end{aligned}\right\} = g(\alpha) = \frac{A}{q}J(T) \tag{10}$$

The intermediate stages of the solutions are given in the Appendix.

## VERSIONS OF THE KINETIC EQUATION SOLUTIONS

### *Version A*

According to eqn. (9), taking into account eqns. (7) and (8), we obtain

$$G(\alpha) = \frac{ART^2}{qE}\mathrm{e}^{-E/RT}[1 - S(T)] + S(T_m) \tag{11}$$

where

$$S(T)=\sum_{N=1}^{\infty}(-1)^{N+1}(N+1)!\left(\frac{RT}{E}\right)^{N} \tag{12}$$

The series (12) is convergent only for $RT/E=0$ ($T=0$). For $0<RT/E<0.3$ its partial sum containing at least the first two terms takes the values in the range

$$\frac{2RT}{E}>S(T)>0 \qquad \text{when } \infty \gg N \geqslant 2 \tag{12'}$$

Similarly, according to eqn. (10) we obtained

$$g(\alpha)=\frac{AR}{qE}\left\{T^2\ \mathrm{e}^{-E/RT}[1-S(T)]-T_p^2\ \mathrm{e}^{-E/RT_p}[1-S(T_p)]\right\} \tag{13}$$

$$\frac{2RT_p}{E}>S(T_p)>0 \tag{13'}$$

After determining the integration constants $C_1$ and $C_2$ we may compare eqns. (12) and (13), as a result of which an absurd dependence is obtained:

$$S(T_m)+\frac{ART_p^2}{qE}\mathrm{e}^{-E/RT_p}[1-S(T_p)]=0(>0) \tag{14}$$

Dependence (14) is also obtained from eqn. (3) or eqn. (10) assuming different upper limits of integration ($\alpha=\alpha_m$, $T=T_m$) and conditions (5), (6), (7) and (8). Some authors accept the value $2RT/E\approx$ constant [2,3], though others omit it completely ($2RT/E\approx 0$ [4,5]), from which it results that $T_p \to 0$. As a result we obtain a simple expression:

$$g(\alpha)=\frac{ART^2}{qE}\mathrm{e}^{-E/RT} \tag{15}$$

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{qE}-\frac{E}{RT} \tag{15'}$$

### *Version B*

According to eqn. (9), taking into account eqns. (7) and (8) we obtain

$$G(\alpha)=\frac{A}{q}T\ \mathrm{e}^{-E/RT}+1-\frac{E}{RT_m} \qquad \text{for } n=1 \tag{16}$$

and according to eqn. (10)

$$g(\alpha)=\frac{A}{q}\left(T\ \mathrm{e}^{-E/RT}-T_p\ \mathrm{e}^{-E/RT_p}\right) \tag{17}$$

In a further procedure, similar to version A, from the comparison of eqns. (16) and (17) we obtain

$$\frac{E}{RT_m} - \frac{AT_p}{q} e^{-E/RT_p} = 1 \qquad T_m > T_p \tag{18}$$

From eqn. (18), by the iteration method, we may try to estimate the value $T_p$, whereas it is more convenient to omit in eqn. (17) the second term in the parentheses and assume that

$$g(\alpha) \approx \frac{AT}{q} e^{-E/RT} \tag{19}$$

$$\ln\frac{g(\alpha)}{T} = \ln\frac{A}{q} - \frac{E}{RT} \tag{19'}$$

*Version C*

According to eqn. (10), assuming $T_p = 0$ and Doyle's approximation [6] (see Appendix) we obtained

$$g(\alpha) = 0.00484\frac{AE}{qR}\ e^{-1.0516\,E/RT} \tag{20}$$

for $20 < E/RT < 60$

$$\ln\ g(\alpha) = \ln\frac{0.00484AE}{qR} - \frac{1.0516E}{RT} \tag{20'}$$

Equations (15), (19) and (20) may be presented in the following linear form:

$$\ln\ g(\alpha) - m\ \ln\ T = \ln\ \text{constant} - \frac{E}{RT}(1 + p) \tag{21}$$

where for $m = 0$, $p = 0.0516$, and for $m = 1$ or $2$, $p = 0$.

The problem was formulated in a similar way by Popescu et al. [7].

*Other versions of the solutions*

According to Horowitz and Metzger [8] or to Fedoseev et al. [9] for $T \ll 2T_m$, an approximation of the subintegral function has been assumed:

$$e^{-E/RT} \simeq e^{E/RT_m}\ e^{E/RT_m^2(T-T_m)}$$

and making use of eqn. (8) we obtained directly

$$g(\alpha) = e^{E/RT_m^2(T-T_m)} \tag{22}$$

However, Van Krevelen et al. [10] assumed for $0.9 < T/T_m < 1.1$ a different approximation of the subintegral function:

$$e^{-E/RT} = e^{-E/RT_m}\left(\frac{T}{T_m}\right)^{E/RT_m}$$

As a result of integrating according to eqn. (10), for $T_p = 0$, we obtained

$$g(\alpha) = \frac{ART_m^2}{q(E+RT_m)} e^{-E/RT_m}\left(\frac{T}{T_m}\right)^{(E+RT_m)/RT_m} \tag{23}$$

However, it should be noted that if $T = T_m$, then $g(\alpha_m) = 1$; thus

$$1 = \frac{ART_m^2}{q(E+RT_m)} e^{-E/RT_m} \qquad \text{or} \quad \frac{RT_m}{E} \approx 0$$

Hence eqn. (23) may also be expressed as

$$g(\alpha) = \left(\frac{T}{T_m}\right)^{(E/RT_m)+1} \tag{24}$$

If in eqn. (22) we assume the approximation

$$\frac{T}{T_m} - 1 \approx \ln\frac{T}{T_m}$$

with the constraint $0 < (T/T_m) \leq 2$, then we obtain a modification in a form close to eqn. (24):

$$g(\alpha) = \left(\frac{T}{T_m}\right)^{(E/RT_m)} \tag{25}$$

The linear forms of eqns. (22) and (24) may additionally be estimated by a compensating calculation for a straight line crossing the point with coordinates (0, 0), which is an obvious advantage of the models

$$\ln g(\alpha) = \frac{E}{RT_m^2}(T - T_m) \tag{22'}$$

$$\ln g(\alpha) = \left(\frac{E}{RT_m} + 1\right)\ln\frac{T}{T_m} \tag{24'}$$

$$\ln g(\alpha) = \frac{E}{RT_m}\ln\frac{T}{T_m} \tag{25'}$$

in which, when $T = T_m$, then $\ln g(\alpha_m) = 0$.

## EXAMPLE

In investigations on the thermal decomposition of D-glucose at a heating rate of $q = 0.5$ K min$^{-1}$ the following average results were obtained [11]: $E = 124.91$ kJ mol$^{-1}$; $\ln A = 30.92$ ($A$ in min$^{-1}$); variable order of reaction $n = 1, 5/4, 3/2, 7/4, 2$.

Determining the degree of conversion defined as

$$\alpha = \frac{\text{mass decrement in the temperature range from } T_P \text{ to } T(\%)}{\text{total mass decrement in the conversion from } T_p \text{ to } T_k(\%)}$$

and assuming, in accordance with the suggestion of the previous investigations, that the reaction order $n$ is two [12], confirmed by condition (7) for $x_m = 0.5$ at a temperature $T_m = 467$ K, the kinetic parameters were searched for ($E$, $\ln A$) making use of suitable equations with various estimating techniques. The results of the calculations are presented in Table 1 and plotted as $\ln A$ vs. $E$ in Fig. 1.

## DISCUSSION AND SUMMARY

The isokinetic effect or the law of compensation [13–15] is expressed by an empirical dependence

$$\ln A = a + bE \tag{26}$$

TABLE 1

Kinetic parameters resulting from regression estimation [a]

| No. | Coordinates | Equation no. | $E$ (kJ mol$^{-1}$) | $\ln A$ | $r^2$ ($\rho^2$) (%) [b] |
|---|---|---|---|---|---|
| 1 | $\ln \alpha' - 2\ln(1-\alpha)$ vs. $\frac{1}{T}$ | 1′ | 147.58 | 34.90 | 96.41 |
| 2 | $\ln\frac{\alpha}{1-\alpha} - 2\ln T$ vs. $\frac{1}{T}$ | 21<br>$m = 2$ $p = 0$ | 133.49 | 31.13 | 99.62 |
| 3 | $\ln\frac{\alpha}{1-\alpha} - \ln T$ vs. $\frac{1}{T}$ | 21<br>$m = 1$ $p = 0$ | 137.36 | 28.59 | 99.64 |
| 4 | $\ln\frac{\alpha}{1-\alpha}$ vs. $\frac{1}{T}$ | 21<br>$m = 0$ $p = 0.0516$ | 134.30 | 31.38 | 99.64 |
| 5 | $\ln\frac{\alpha}{1-\alpha}$ vs. $T - T_m$ | 22′ | 141.79 | 33.28 | (99.72) |
| 6 | $\ln\frac{\alpha}{1-\alpha}$ vs. $\ln\frac{T}{T_m}$ | 24′ | 141.56 | 33.24 | (99.66) |
| 7 | $\ln\frac{\alpha}{1-\alpha}$ vs. $\ln\frac{T}{T_m}$ | 25′ | 137.68 | 33.24 | (99.66) |

[a] Data as reported previously [11].

[b] The values $r^2$ describe the statistical determination for a straight line plot not crossing (0, 0); $\rho^2$ values (in parentheses) are for straight line plots crossing (0, 0).

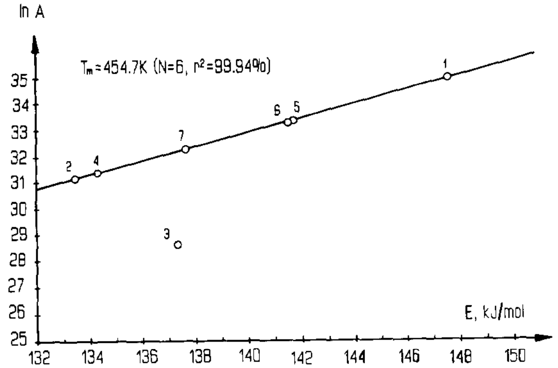


Fig. 1. Estimated kinetic parameters plotted as ln *A* vs. *E*.

In general, dependence (26) refers to the same chemical reaction but with the reaction taking place under changed conditions [13,14], or to substances with similar chemical structures, e.g. complex compounds, coal tar, pitch etc. [14,15].

From Arrhenius' law or from condition (8) we may derive the equations that explain the linear form of eqn. (26):

$$\ln A = \ln k_m + \frac{E}{RT_m} \tag{27}$$

$$\ln A = \ln \frac{qE}{RT_m^2} + \frac{E}{RT_m} \tag{8'}$$

in which the subscript *m* refers to the maximum rate of the reaction. Especially interesting for both eqns. (27) and (8′) is the formulation (Fig. 1)

$$\frac{\partial \ln A}{\partial E} = \frac{1}{RT_m} \tag{26'}$$

from which it results that for the solutions fulfilling eqn. (26), it is possible to determine the temperature of the maximum rate of the reaction. Thus, in accordance with the example given, $T_m = 467$ K was determined, and from eqn. (26) $T_m = 454.7$ K ($\Delta T_m = 12.3$ K) was calculated. Equation (26) confirms only the correctness of the estimations of the parameters of eqn. (1). In general, a straight line with a very high coefficient of correlation is obtained through an assessment of parameters according to several equations, viz. eqns. (15), (20), (22), (24), (25), and possibly eqn. (1′) (with eqn. (6)). It may be shown that a small deviation of the estimations from the straight line (eqn. (26)) affects very strongly the value of $T_m$ even by some tens of degrees Kelvin. Thus we should not assume that the dependence analysed is unrestricted.

In eqn. (10) it may also be easily seen that the right-hand side of the equation is the product of a very large quantity ($A$) and a very small one $J(T)$—the imperfections arising from the solution of the integral affect the remaining estimated quantities. It is only fitting to remark that one more formal meaning has been ascribed to eqn. (26).

To make use of the information from eqn. (26), the solution of the integral of eqn. (15) has been modified through the introduction of the temperature $T_m$ [8–10], e.g. by multiplying both sides of the equation by the factor $T_m^2$. After applying condition (8) we obtain the form

$$g(\alpha) = \left(\frac{T}{T_m}\right)^2 \exp\left[\frac{E}{RT_m}\left(1 - \frac{T_m}{T}\right)\right] \tag{28}$$

which for practical purposes it is convenient to present in the form

$$\ln g(\alpha) + 2 \ln\frac{T_m}{T} = \frac{E}{RT_m}\left(1 - \frac{T_m}{T}\right) \tag{28'}$$

or

$$\left(\ln g(\alpha) + 2 \ln\frac{T_m}{T}\right) \text{ vs. } \left(1 - \frac{T_m}{T}\right)$$

Dependence (28′) may be estimated similarly to the forms (22′), (24′) and (25′). Figure 2 presents the example analysed in the coordinates (28′).

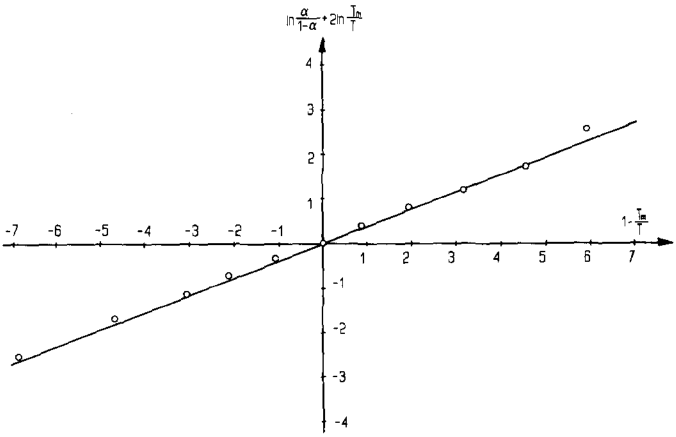


Fig. 2. Relationship between $(\ln(\alpha/(1-\alpha)) + 2\ln(T_m/T))$ and $(1-(T_m/T))$ values.

After certain transformations it is also possible to demonstrate a close relationship between eqns. (28) and (24) or (25), namely at the constraint $0 < (T_m/T) \leqslant 2$ the approximation

$$1 - \frac{T_m}{T} \approx -\ln\frac{T_m}{T}$$

reduces eqn. (28) to the form

$$g(\alpha) = \left(\frac{T}{T_m}\right)^{(E/RT_m + 2)} \tag{29}$$

Finally, the solution of the kinetic temperature equation (eqn. (1)) with due consideration to condition (8), may be presented in the form of a general mathematical equation:

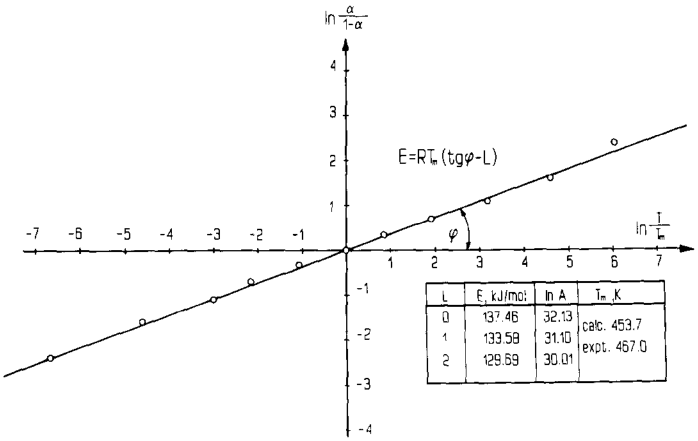
$$g(\alpha) = \left(\frac{T}{T_m}\right)^{(E/RT_m) + L}$$

We may thus obtain the forms of equations presented by different authors: from eqn. (22), $L = 0$ (Horowitz–Metzger [8,9]); from eqn. (24) $L = 1$ (Van Krevelen et al. [10]); from eqn. (15) $L = 2$ (Coats–Redfern [2,3] in the formulation presented in the present paper (eq. (28)).

Thus it is possible to make an assessment of the calculations of the activation energy presented by Zsakó [14], and of the considerations of Agrawal [16] on the compensating effect resulting from the mathematical formalism assumed.

The exponent $(E/RT_m) + L$ explains the "variability" of the activation energy on account of parameter $L$, namely (Fig. 3)

$$E = RT_m(tg\varphi - L)$$



| L | E, kJ/mol | ln A | $T_m$, K |
|---|---|---|---|
| 0 | 137.46 | 32.13 | calc. 453.7<br>expt. 467.0 |
| 1 | 133.58 | 31.10 | |
| 2 | 129.69 | 30.01 | |

Fig. 3. Geometric meaning of the $L$ parameter and its influence on the estimated kinetic parameters $E$ and $A$.

Correspondingly, from condition (8) we obtain

$$\ln A = \ln\frac{q}{T_m} + tg\varphi - L + \ln(tg\varphi - L)$$

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## APPENDIX

It may be shown that the integrals presented in eqns. (9) and (10)

$$I(T) = \int e^{-E/RT}\, dT \tag{A1}$$

$$J(T) = \int_{T_p}^{T} e^{-E/RT}\, dT \tag{A2}$$

can be reduced to version A, B or C by using the substitution

$$u = E/RT \qquad u_p = E/RT_p \qquad dT = -(E/RT)u^{-2}\, du$$

*Version A*

$$I(T) = -\frac{E}{R}\int e^{-u}u^{-2}\, du \tag{A3}$$

$$J(T) = \frac{E}{R}\left(\int_{u}^{\infty} e^{-u}u^{-2}\, du - \int_{u_p}^{\infty} e^{-u}u^{-2}\, du\right) \tag{A4}$$

Using the procedure of $n$-fold integration by parts ($\int \mathrm{e}^{-u}\,\mathrm{d}u$) one obtains a solution expressed by means of an asymptotic series

$$I(T)=\frac{E\,\mathrm{e}^{-u}}{Ru^2}\left(1-\frac{2!}{u}+\frac{3!}{u^2}-\frac{4!}{u^3}\right)+Q \tag{A5}$$

where

$$Q=\left(\frac{E}{R}\right)(-1)^{s+1}s!\int \mathrm{e}^{-u}u^{-(s+2)}\,\mathrm{d}u \qquad \text{for } s=4$$

while for $s>4$

$$\lim_{s\to\infty} Q=0$$

As a result we obtain

$$I(T)=\frac{RT^2}{E}\mathrm{e}^{-E/RT}[1-S(T)] \tag{A6}$$

and correspondingly

$$J(T)=\frac{RT^2}{E}\mathrm{e}^{-E/RT}[1-S(T)]-\frac{RT_p^2}{E}\mathrm{e}^{-E/RT_p}[1-S(T_p)] \tag{A7}$$

where $S(T)$ is expressed by eqn. (12).

*Version B*

$$I(T)=-\frac{E}{R}[-\mathrm{e}^{-u}u^{-1}-Ei(-u)] \tag{A8}$$

where [17]

$$Ei(-u)=\int \mathrm{e}^{-u}u^{-1}\,\mathrm{d}u$$

According to ref. 18 for large values of $u$ ($u>5$) we have

$$-Ei(-u)=\mathrm{e}^{-u}u^{-1}\left(1-\frac{1!}{u}+\frac{2!}{u^2}-\frac{3!}{u^3}+\dots\right) \tag{A9}$$

We obtain eqn. (A6) by inserting the series (A9) into eqn. (A8), but with the approximation $(u+1)/u\approx 1$ in eqn. (A8) we integrate by the parts $\int \mathrm{d}u$ and obtain

$$Ei(-u)=\mathrm{e}^{-u}+\int \mathrm{e}^{-u}\left(\frac{u+1}{u}\right)\mathrm{d}u\approx 0 \tag{A10}$$

Finally

$$I(T)=T\,\mathrm{e}^{-E/RT} \tag{A11}$$

and, correspondingly

$$J(T) = T\ \mathrm{e}^{-E/RT} - T_p\ \mathrm{e}^{-E/RT_p} \qquad \text{(A12)}$$

*Version C*

It may be shown for the integral (31) that when $T_p = 0$

$$J(T) = \frac{E}{R}\int_u^{\infty} \mathrm{e}^{-u}u^{-2}\ \mathrm{d}u = \frac{E}{R}p(u) \qquad \text{(A13)}$$

According to Doyle [6] the function $p(u)$ is expressed as

$$\lg\ p(u) = -2.315 - 0.4567u \qquad \text{for } 20 < u < 60 \qquad \text{(A14)}$$

and thus

$$p(u) = 0.00484\ \mathrm{e}^{-1.0516u} \qquad \text{where } u = \frac{E}{RT} \qquad \text{(A15)}$$

## LIST OF SYMBOLS

| | |
|---|---|
| $a$, $b$ | constants in eqn. (26) |
| $A$ | coefficient of frequency (min$^{-1}$) |
| $C$, $C_1$, $C_2$ | constants of integration |
| $Ei(-u)$ | Euler's function |
| $E$ | activation energy (J mol$^{-1}$) |
| $f(\alpha)$ | function symbol of the argument $\alpha$ |
| $g(\alpha)$, $G(\alpha)$ | weight integrals |
| $I(T)$ | indefinite integral of argument $T$ |
| $J(T)$ | definite integral of argument $T$ |
| $k$ | rate constant (min$^{-1}$) |
| $n$ | order of the reaction |
| $N$ | natural value |
| $p(u)$ | approximating function of Doyle according to ref. 6 |
| $q$ | rate of heating (K min$^{-1}$) |
| $r$, ($\rho$) | coefficient of correlation of straight line (crossing point with coordinates (0, 0)) ($\rho$) |
| $R$ | universal gas constant, $R = 8.314$ J mol$^{-1}$ K$^{-1}$ |
| $T$ | absolute temperature (K) |
| $x$ | normalized mass decrement, $x \in \langle 1, 0 \rangle$ |
| $\alpha$ | degree of transformation, $\alpha \in \langle 0, 1 \rangle$ |
| $\alpha'$ | reaction rate, $\alpha' = \mathrm{d}\alpha/\mathrm{d}T$ (K$^{-1}$) |
| $\varphi$ | angle of inclination of the straight line |
| $\tau$ | time (min) |

## Subscripts

| | |
|---|---|
| $k$ | final conditions |
| $m$ | maximum reaction rate |
| $p$ | initial conditions |