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On the Temperature Corresponding to α = 0.632 in Non-isothermal JMA Kinetics

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The expression for rate, $\mathrm{d}\alpha/\mathrm{d}T$, of the nucleation and growth (NG) process under non-isothermal conditions, as described by the Johnson-Mehl-Avrami (JMA) kinetic model, served as the basis for a detailed study of a class of functions $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$, where $m \in \Re$. Studies of the fractional conversion, α, of the NG process at the temperature of the maximum of function $\Phi(m)$, $T = T(m)$, have shown that when reduced activation energy, $x = E/RT$, approaches infinity ($x \to \infty$), fractional conversion, α, at the temperature corresponding to the maximum of function $\Phi(m)$, α(m), converges to α = 0.632, for any value of *m*. It has been further shown that fractional conversion, α, for the NG process is equal to α = 0.632 at the temperature corresponding to the maximum of function $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$ for the particular value of parameter *m* from the interval: $1 \le m \le 2$.

INTRODUCTION

The well known work of Criado and Ortega,[1] Gao, Chen and Dollimore,[2] and Malek[3–5] has shown that fractional conversion, α_p, of the non-isothermal NG process described by the JMA kinetic model, at the temperature of the maximum rate of the NG process, T_p, is less than 0.632. However, the exact temperature corresponding to the fractional conversion, α = 0.632, has not been established yet.

In order to improve kinetic analysis, the product of functions has been applied,[1–9] for example Malek's function $z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}T)T^2$. This function can be considered as a special case of the functions with the general form $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$ when $m = 2$. The concept of function $\Phi(m)$ is somewhat analogous to the assisting function φ introduced previously in the analysis of isothermal kinetic processes:[10]

$$\Phi = F\varphi \tag{1}$$

The relationship between function $\Phi(m)$ and JMA function is illustrated in Figure 1. If the function $\Phi = \Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$ has the maximum for a selected value of *m* at temperature $T(m)$, then at the same temperature the JMA kinetic model function has the degree of conversion $\alpha(m)$. For $m = 0$, it follows that $T(m{=}0) = T_p$, and function $\Phi(m{=}0)$ is identical with the JMA curve. Also, for this special case $\alpha(m{=}0) = \alpha_p$. In all other cases, *i.e.,* for $m \neq 0$, the temperature of the maximum of curve $\Phi(m)$ is different from the temperature of the maximum of the JMA curve ($T(m \neq 0) \neq T_p$). Therefore, fractional conversion of the JMA process at that temperature is different from α_p, *i.e.*, ($\alpha(m \neq 0) \neq \alpha_p$), and corresponds to the temperature of the maximum of Φ-function only, while $T(m)$ and $\alpha(m)$ are parameters of the JMA function.

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In this article, the analysis of the class of functions of the general form: $\Phi(m) = (d\alpha/dT)T^m$ (where the value of parameter m is chosen at will) has shown that the temperature corresponding to the fractional conversion $\alpha = 0.632$ corresponds to the maximum of function $\Phi(m)$, where the particular value of m lies in the interval: $1 \leq m \leq 2$.

THEORETICAL

The reaction rate of a solid-state process is usually described by the following differential equation based on the isokinetic hypothesis and Arrhenius temperature dependency:[11]

$$\frac{da}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where α is the fractional conversion at time t and $f(\alpha)$ is an arbitrary kinetic model equation (*e.g.*, $n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$). A is the pre-exponential factor, E is the activation energy for crystallization, R is the gas constant and T is absolute temperature.

Assuming a constant heating rate, β, that is $T = T_i + \beta t$ and $dT = \beta dt$, $g(\alpha)$ (integral form of kinetic equation) is calculated by integration of Eq. (2):

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{Z}{\beta}\int_{T_i}^{T}\exp\left(-\frac{E}{RT}\right)dT \cong \frac{Z}{\beta}I_A \tag{3}$$

The integral:

$$I_A = \int_{T_i}^{T}\exp\left(-\frac{E}{RT}\right)dT \tag{4}$$

is called the Arrhenius integral. Z is the pre-exponential factor, and in this work it has been assumed to be temperature independent.

By substituting $x = E/RT$ (reduced activation energy), Eq. (4) yields:

$$I_A = \frac{E}{R}\int_x^{\infty}\frac{\exp(-x)}{x^2}dx\,. \tag{5}$$

It is well known that the Arrhenius integral (I_A) cannot be calculated exactly and is therefore expressed by an approximate function; the most common approximation is Eq. (6):

$$I_A = \frac{E}{R}\frac{\pi(x)}{x}\exp(-x) \tag{6}$$

where $\pi(x)$ denotes the function related to the integral in Eq. (5). With Eq. (6), the integral form of kinetic equation (3) reads:

$$g(\alpha) = \frac{ZE}{\beta R}\frac{\pi(x)}{x}\exp(-x) = \exp\left\{-x + \ln\left(\frac{\pi(x)}{x}\right) + \ln\left(\frac{ZE}{\beta R}\right)\right\} \tag{7}$$

If the nucleation and growth process (NG) could be described by the JMA equation, $g(\alpha) = (-\ln(1-\alpha))^{1/n}$, for the rate of NG process, one can write:

$$\frac{d\alpha}{dT} = \frac{dI}{dT}\exp(-I) \tag{8}$$

where:

$$I = \exp\left\{-nx + n\ln\left(\frac{\pi(x)}{x}\right) + n\ln\left(\frac{ZE}{\beta R}\right)\right\} \tag{9}$$

Since:

$$\frac{dI}{dT} = \left\{\frac{nE}{RT^2} + n\frac{d}{dT}\left[\ln\left(\frac{\pi(x)}{x}\right)\right]\right\}I \tag{10}$$

$$\frac{dI}{dT} = \left\{\frac{nE}{RT^2} - n\frac{x}{\pi(x)}\left[\frac{\pi'(x)}{x} - \frac{\pi(x)}{x^2}\right]\frac{E}{RT^2}\right\}I \tag{11}$$

$$\frac{dI}{dT} = \frac{nE}{RT^2}(1+\mu(x))I \tag{12}$$

where:

$$\mu(x) = \frac{1}{x} - \frac{\pi'(x)}{\pi(x)} \tag{13}$$

it follows:

$$\frac{d\alpha}{dT} = \frac{nE}{RT^2}(1+\mu(x))I \tag{14}$$

There are a number of methods for determination of the $\pi(x)$ values. In some of them asymptotic series and complex approximations for $\pi(x)$ are used.[11–14] Flynn[15] criticized some of the approximations, as he considers complex approximation[16] to be far better. There are first to fourth degree rational approximations for the Arrhenius integral. The first degree rational approximation is the Gorbachev[17] function with $\pi(x) = 1/(x+2)$, and the fourth degree rational approximation is by Senum and Yang[16] »with an accuracy better than 10^{-5} % for $x \geq 20$«:[18,19]

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{15}$$

For small values[15,16] of x, the Arrhenius integral may be better expressed by using the power series expansion:

$$I_{\mathrm{A}} = \frac{E}{R}\left(\frac{\exp(-x)}{x} + \gamma + \ln x + \sum_{n=1}^{\infty}\frac{(-1)^n x^n}{mn!}\right) \quad (16)$$

By coupling Eqs. (6) and (16), $\pi(x)$ can be defined as:

$$\pi(x) = 1 + \left(\gamma + \ln x + \sum_{n=1}^{\infty}\frac{(-1)^n x^n}{nn!}\right) x \exp(x) \quad (17)$$

where γ = 0.5772156649 (Euler-Mascheroni constant). The desired accuracy can be achieved by truncating the number of terms in the series.

Equations (15) and (17) can be used to calculate values for $\pi(x)$ over the whole range of x (Table I). Table I gives the values of $\pi(x)$, calculated at five decimals. Calculated values are checked against the tabulated values of Gautschi and Cahill[20] and a very good match has been found.

As known, Doyle's approximation presumes the same activation energy correction for a wide range of x values.[21] For $28 < x < 50$ the correction factor is equal to 1.052, whereas for $18 < x < 35$ the correction factor is equal[15] to 1.075. However, Doyle also carried out a function changing the correction factors continuously, resulting in $E/(x\pi(x))$ instead of E*const.[21] In this work, a new expression for continuous correction has been obtained in deriving $\mathrm{d}I/\mathrm{d}T$ and it reads: $E*(1 + \mu(x))$ (Eq. 12). The two mentioned expressions for continuous correction are in full agreement, which is confirmed by equation $(1 + \mu(x)) = 1/(x\pi(x))$ (Eq. A4).

Application of Function Φ(m) *to the Differential Form of the JMA Kinetic Model*

If $\Phi(m)$-function is expressed as:

$$\Phi(m) = \frac{d\alpha}{dT}T^m = \frac{nE}{R}(1+\mu(x))I\exp(-I)T^{m-2} \quad (18)$$

then for $\mathrm{d}\Phi/\mathrm{d}T = 0$ one obtains (Eq. A6–A9):

$$nx(1+\mu(x))(-\ln(1-\alpha(m))-1) = m - x\mu(x) \quad (19)$$

Equation (19) can be rearranged in (Eq. A4):

$$n(-\ln(1-\alpha(m))-1) = [m - x\mu(x)]\pi(x) \quad (20)$$

In some early works, it was accepted that at the maximum of the JMA curve α_p = 0.632. Criado and Ortega,[1] Gao, Chen and Dollimore,[2] and Malek[3,5] rejected this wrong assumption. They have shown that fractional conversion at the maximum of the JMA curve is always smaller than 0.632, even for large values of x (as illustrated by α_p values in Table II).

In this work, the analysis of α values has been extended beyond the maximum of the JMA curve in order to find out the position of α = 0.632 for cases other than $x\to\infty$. From the above cited works it is obvious that α is equal to 0.632 at temperatures higher than that corresponding to the maximum of the experimental JMA curve, but the position of α = 0.632 has not been established.

TABLE I. Values of $\pi(x)$, $x\pi(x)$, $\mu(x)$ and $x\mu(x)$ to five decimal places

x	$\pi(x)$[a]	$x\pi(x)$	$\mu(x)$	$x\mu(x)$
$x\to0$	1	0	∞	1
0.01	0.95921	0.00959	103.251	1.03251
0.1	0.79854	0.07985	11.5229	1.15229
0.5	0.53854	0.26927	2.71371	1.35686
1	0.40365	0.40365	1.47738	1.47738
2	0.27734	0.55469	0.80282	1.60565
3	0.21375	0.64125	0.55946	1.67839
4	0.17462	0.69847	0.43170	1.72681
5	0.14789	0.73945	0.35236	1.76182
6	0.12839	0.77037	0.29809	1.78851
7	0.11351	0.79459	0.25852	1.80962
8	0.10176	0.81410	0.22835	1.82677
9	0.09224	0.83018	0.20456	1.84100
10	0.08437	0.84367	0.18530	1.85302
12	0.07209	0.86504	0.15602	1.87224
14	0.06294	0.88123	0.13478	1.88695
16	0.05587	0.89393	0.11866	1.89856
18	0.05023	0.90416	0.10600	1.90802
20	0.04563	0.91258	0.09579	1.91584
25	0.03713	0.92831	0.07722	1.93057
30	0.03131	0.93942	0.06470	1.94088
35	0.02706	0.94726	0.05567	1.94852
40	0.02384	0.95342	0.04886	1.95441
45	0.02130	0.95828	0.04354	1.95908
50	0.01924	0.96223	0.03926	1.96289
60	0.01614	0.96823	0.03281	1.96871
70	0.01389	0.97259	0.02818	1.97294
80	0.01220	0.97589	0.02470	1.97617
90	0.01087	0.97849	0.02199	1.97871
100	0.00981	0.98058	0.01981	1.98076
200	0.00495	0.99015	0.00995	1.99019
500	0.00199	0.99602	0.00399	1.99603
$x\to\infty$	0	1	0	2

[a] $\pi(x)$ values for $x < 9$ are calculated according to Eq. (17) using 40 members of infinite row expansion. $\pi(x)$ for $x \geq 9$ are calculated according to Eq. (15).

TABLE II. A series of non-isothermal JMA kinetic curves (n = 2) were simulated in such a way that fractional conversion α = 0.632 occurs at T_0 = 1100.0 K as the value of reduced activation energy at that temperature changes to give x_0 = 2 to x_0 = 200

x_0	E_a / kJ mol^{-1}	$T_p(m=0)$ / K	$\alpha_p(m=0)$	$T(m=1)$ / K	$\alpha(m=1)$	$T(m=2)$ / K	$\alpha(m=2)$
2	18.29	1063.3	0.542	1086.8	0.600	1108.2	0.652
5	45.73	1088.8	0.581	1095.3	0.611	1101.4	0.639
10	91.45	1096.2	0.602	1098.3	0.619	1100.3	0.634
20	182.9	1098.9	0.616	1099.5	0.624	1100.0	0.633
50	457.3	1099.8	0.625	1099.9	0.629	1100.0	0.632
100	914.5	1099.9	0.629	1100.0	0.630	1100.0	0.632
200	1829	1100.0	0.630	1100.0	0.631	1100.0	0.632

From Eq. (20), it follows that:

$$\pi(x)[m - x\mu(x)] = 0 \tag{21}$$

if

$$-\ln(1-\alpha(m)) - 1 = 0 \tag{22}$$

i.e., α = 0.632. Equation (21) is satisfied when $\pi(x) \to 0$ or/and $[m - x\mu(x)] \to 0$.

If $x \to \infty$, then $\pi(x) \to 0$ (Table I) regardless of the values of m. It means that as $x \to \infty$ all functions $(\mathrm{d}\alpha/\mathrm{d}T)T^m$ have $\alpha(m)$ = 0.632 regardless of the values of m (Figure 2a). From Figure 2a, it can be seen that as reduced activation energy, x, increases, the value of the product $\pi(x)[m - x\mu(x)]$ approaches zero and consequently fractional conversion at the maximum, α, approaches 0.632 (Figure 2a).

It follows from Eqs. (20)–(22) that 0.632 is the characteristic value of α for the JMA kinetic model and, also, that this value does not depend on n, while all the other fractional conversions depend on n. The mentioned equations comprise the core of the present work. They show that α = 0.632 for all the m-values for which $[m - x\mu(x)] = 0$. Since it is unlikely that the x-value (and thus $x\mu(x)$) is known in advance, only a span can be determined within which the m-value lies. It is essential that Eqs. (20)–(22) comprise the dependence of m-values on x-values. This dependence refines Malek's conclusion according to which α = 0.632 occurs at the maximum of $z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}T)T^2$ function.

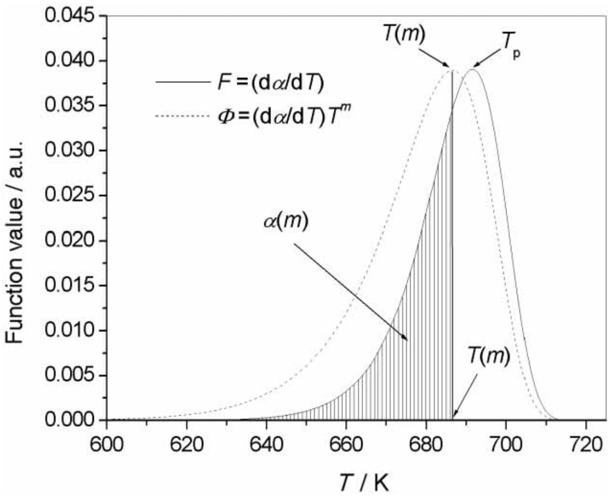

Figure 1. The differential form of the JMA function, $F = (\mathrm{d}\alpha/\mathrm{d}T)$, describing the rate of the nucleation and growth process (full line) and normalized function $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$ (dashed line). At the temperature of the maximum of function $\Phi(m)$, the JMA function has the degree of conversion $\alpha(m)$ (hatched) corresponding to temperature $T(m)$.

Precisely, if $m < 1$ the α-values increase and if $m \geq 2$ the α-values decrease towards α = 0.632 with an increase of reduced activation energy (Table II and Figure 2a.). This fact was previously established only for m = 2 (Malek's z function)[5].

Situations $x \to 0$ or $x \to 8$ are not realistic. Those are limiting cases and it is better to consider the situations for »small values of x« or »large values of x«. In this case $(0 < x < 8)$ $0 < \pi(x) < 1$, and only the equation $m - x\mu(x) = 0$ is decisive for α = 0.632. From Eqs. (21)–(22) it follows that for every value of x there is a value

$$m = M = x\mu(x) \tag{23}$$

This is illustrated in Figure 2b for three different values of M. As shown in Figure 2b, the curves within the range $1 \leq m \leq 2$ intercept the abscissa for finite x, *i.e.* $m = M = x\mu(x)$.

Fractional conversion α = 0.632 occurs at the temperature of the maximum of function $\Phi(m)$ where the value of m is given by Eq. (23). It means that α = 0.632 is obtained for $T(m=M)$. Since the possible values of the product $x\mu(x)$ are

$$1 \leq x\mu(x) \leq 2 \tag{24}$$

If the limit of x approaches zero, the value of $x\mu(x)$ approaches 1, and if the limit of x approaches infinity, the value of $x\mu(x)$ approaches 2 (Table I). It follows:

$$T(m=1) \leq T(m=M) \leq T(m=2) \tag{25}$$

and

$$\alpha(m=1) \leq \alpha(m=M) \leq \alpha(m=2) \tag{26}$$

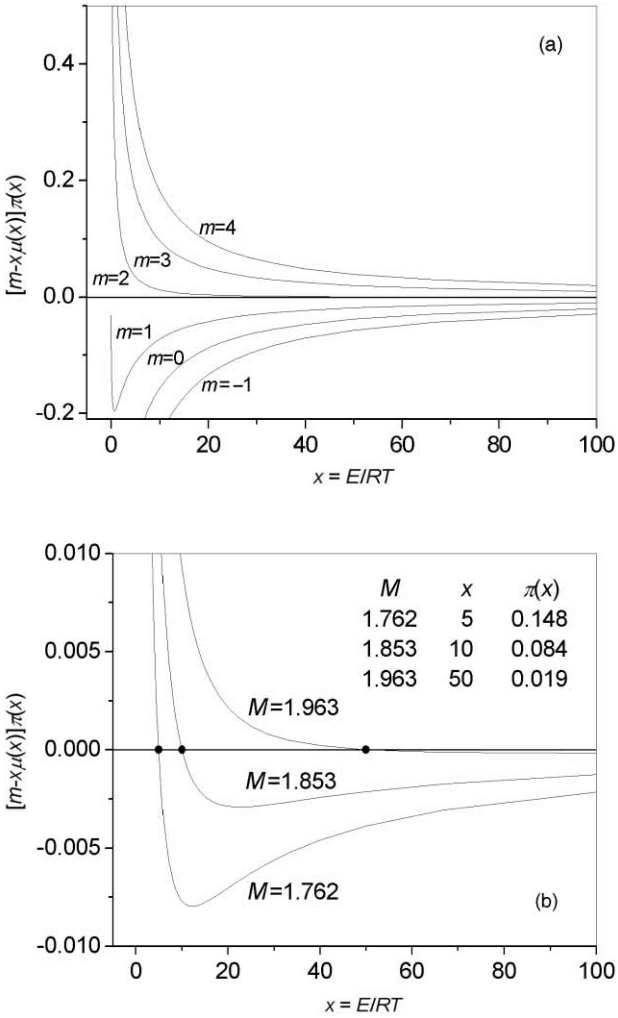

Figure 2. a) Graphical illustration of Eq. (20). It is shown that as $x \rightarrow \infty$, $[m\text{-}x\mu(x)]\pi(x) \rightarrow 0$, and therefore, $\alpha \rightarrow 0.632$. b) Only for values of parameter m: $1 \leq m \leq 2$ curves intercept the abscissa. Namely, for $M = 1.762$, $M = 1.853$ and $M = 1.963$ the curves intercept the abscissa at $x = 5$. 10 and 50, respectively (Table I).

As shown in Figure 3, the value of M is between 1 and 2. The $\Phi(M)$ function has the maximum at temperature $T(M)$, where the JMA function has fractional conversion equal to $\alpha = 0.632$ (hatched). Therefore, the temperature corresponding to $\alpha = 0.632$ could be obtained by determining the maximum of $(\mathrm{d}\alpha/\mathrm{d}T)*T^M$ function, where $M = x\mu(x)$.

TESTING AND DISCUSSION

To test the derived equations, 7 basic functions in the span from $x_0 = 2$ to $x_0 = 200$ have been formed. For every function $T_0 = 1100$ K has been taken, which according to Eq. (9) gives $I = 1$. Activation energy has been determined from $E = x_0RT_0$. In this way, the basic parameters are defined, which enables simulation of 7 different JMA curves. Characteristic values for these 7 functions are listed in Table II (x_0, E, T_p and α_p). In addition, all relevant data for model systems, *i.e.,* $(\mathrm{d}\alpha/\mathrm{d}T)$, $(\mathrm{d}\alpha/\mathrm{d}T)T$ and $(\mathrm{d}\alpha/\mathrm{d}T)T^2$, are given. These systems, besides $x_0 = E/(RT_0)$ and $T_0 = 1100$ K, include also a constant member (as follows from Eq. 9):

$$n \ln\left(\frac{ZE}{\beta R}\right) = \frac{nE}{RT_0} - n \ln\left(\frac{\pi(x_0)}{x_0}\right) \tag{27}$$

and $n = 2$. All T_p and $T(m)$ values in Table II are determined as follows: T_p values are temperatures of the maximum of simulated curves on the basis of JMA functions $(\mathrm{d}\alpha/\mathrm{d}T)(m{=}0)$. T-values for $m = 1$ and $m = 2$ are obtained by determination of the maximum of curves $(\mathrm{d}\alpha/\mathrm{d}T)T$ and $(\mathrm{d}\alpha/\mathrm{d}T)T^2$. All the α-values (Table II) are calculated from Eq. (28):

TABLE III. Values of $T(m{=}M)$ for the Φ-functions calculated using simulated non-isothermal JMA curves given in Table II

x_0	M	$T(m{=}M)^{(a)}$	$T(m{=}M) \approx T_p{+}\Delta T$ [(b)]	T_0 [(c)]
2	1.606	1101.7	1098.7	1100.0
5	1.762	1099.6	1099.9	1100.0
10	1.853	1099.7	1100.0	1100.0
20	1.916	1099.9	1100.0	1100.0
50	1.963	1100.0	1100.0	1100.0
100	1.980	1100.0	1100.0	1100.0
200	1.990	1100.0	1100.0	1100.0

(a) Eq. (29), (b) Eq. (30), (c) Eq. (31).

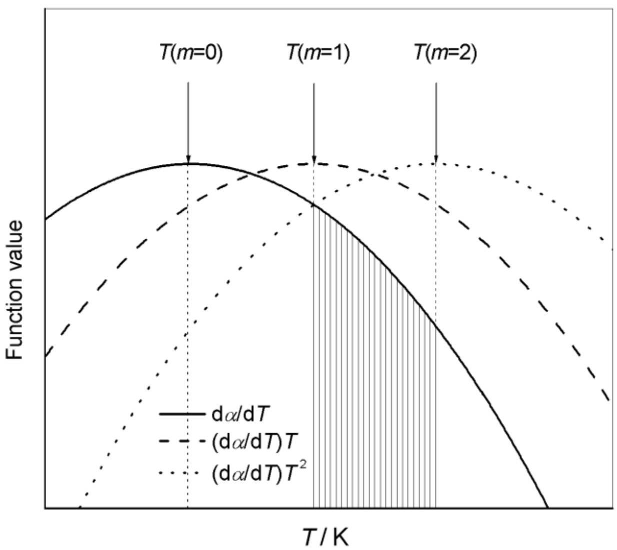

Figure 3. Details of normalized Φ-functions for $m = 0$, 1 and 2.

TABLE IV. Different approaches to the problem of α=0.632

Early works[22]	The position of α = 0.632 is at the maximum of JMA curve (α_p = 0.632).
Criado and Ortega;[1] Gao, Chen and Dollimore;[2] Malek[3]	If x is not infinite, α-values at the maximum of JMA curve are always smaller than 0.632. If $x \to \infty$, α = 0.632.
Malek[5]	Function $z(\alpha) = (\mathrm{d}\alpha/\mathrm{d}T)^*\mathrm{T}^2$ is introduced. The maximum of $z(\alpha)$ function corresponds to the TA peak for infinite x.
This work	Function $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)^*T^m$ is introduced. α = 0.632 is obtained for $x \to \infty$ and for $M = x\mu(x)$, where $\alpha(m{=}1) < \alpha(m{=}M) = 0.632 < \alpha(m{=}2)$. This means that α = 0.632 is always at a temperature between $T(m{=}1)$ and $T(m{=}2)$ for $0 < x < \infty$. $T(M) = T_0$.

$$\alpha(m) = 1\text{–}\exp\left\{-\frac{[m - x\mu(x)]\pi(x)}{n} - 1\right\} \tag{28}$$

where the corresponding value of x is calculated from: $x = x_0 T_0 \,/\, T(m)$.

It follows from the theoretical part that the determination of temperature corresponding to α = 0.632 has been reduced to the determination of the maximum of the $(\mathrm{d}\alpha/\mathrm{d}T)^*T^M$ function.

The calculation of $(\mathrm{d}\alpha/\mathrm{d}T)T^M$ is difficult for $1 \le M \le 2$. It has been observed that in this case satisfactory values for $T(m{=}M)$ (where α = 0.632) could be obtained according to:

$$\frac{C}{T(m{=}1)} + \frac{1-C}{T(m{=}2)} = \frac{1}{T(m{=}M)} \tag{29}$$

where C = constant. In this manner, the approximation of x could be obtained. Further calculation could be performed through $T(m{=}M) \approx T_\mathrm{p} + \Delta T$, where:

$$\Delta T = \frac{\pi_p T_p}{n}\left\{\exp\left(\frac{1-\pi_p x_p}{n}\right) - 1\right\} \tag{30}$$

Table III give values for $T(M)$ according to Eq. (29) with C = 0.3 and Eq. (30), as well as the best values obtained as the maximum of the expression:

$$\Phi(M) = \left(\frac{d\alpha}{dT}\right)T^M \tag{31}$$

which always gives $T(M) = T_0$ (Eq. 31).

Each simulated curve has M for which function $\Phi(M) = (\mathrm{d}\alpha/\mathrm{d}T)T^M$ has the maximum at $T(M)$ where for the simulated curve α = 0.632 (Table III). $\alpha(M)$ is between $\alpha(m{=}1)$ and $\alpha(m{=}2)$, and $T(M)$ between $T(m{=}1)$ and $T(m{=}2)$. All the functions $(\mathrm{d}\alpha/\mathrm{d}T)T^m$ for $M < m \le 2$ have maxima at $T = T(m)$, for which α of the JMA curve is greater than 0.632. All the functions $(\mathrm{d}\alpha/\mathrm{d}T)T^m$ for $1 \le m < M$ have maxima at $T = T(m)$ for which α of JMA the curve is less than 0.632.

These facts give a new insight into the position of α = 0.632, as shown in Table IV, where previous findings concerning this problem are chronologically listed.

The results outlined in the last row of Table IV, are based on Eq. (21).

CONCLUSIONS

The class of functions of the general form: $\Phi(m) = (\mathrm{d}\alpha/\mathrm{d}T)T^m$, where α is fractional conversion of the non-isothermal process described by the JMA kinetic model and m parameter with a value chosen at will, was analyzed concerning the position of the function maximum taking into consideration reduced activation energy, x.

It has been shown that as $x \to \infty$ all functions $(\mathrm{d}\alpha/\mathrm{d}T)T^m$ have maxima at $\alpha(m) \to 0.632$ regardless of the values of m. With an increase of reduced activation energy α-values increase towards 0.632 for $m \le 1$, and decrease towards 0.632 for $m \ge 2$.

It has been shown for $1 \le m \le 2$ that the temperature for which $\alpha = 0.632$ of function $(\mathrm{d}\alpha/\mathrm{d}T)$ occurs at $M = x\mu(x)$ of $\Phi(m)$.

Thus, for every value of x, regardless of its being small or large, there is $M = x\mu(x)$, a parameter of the generalized function $\Phi(m)$, giving a particular function $\Phi(M)$ that has a maximum at temperature $T(M)$ for which $\alpha = 0.632$. The α-value equal to 0.632 always occurs at temperatures between $T(m{=}1)$ and $T(m{=}2)$, for $0 < x < \infty$.

The exact temperature $T(M)$ corresponding to the fractional conversion $\alpha(M) = 0.632$ can be determined only if the value of the reduced activation energy, x, is known.

At the current state of measurement techniques, these findings are of little help in the determination of kinetic parameters but offer a contribution to a better understanding of the properties of the JMA kinetic model in non-isothermal conditions.

APPENDIX

Going from Eq. (17) which reads:

$$\pi(x) = 1 + \left(\gamma + \ln x + \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{nn!}\right) x \exp(x) \quad \text{(A1)}$$

and its derivative, by taking into account:

$$\sum_{n=1}^{\infty} \frac{(-1)^n x^n}{n!} = \exp(-x) - 1$$

one obtains:

$$\frac{d\pi}{dx} = \pi'(x) = \frac{(1+x)\pi(x) - 1}{x} \quad \text{(A2)}$$

i.e.,

$$\frac{\pi'(x)}{\pi(x)} = 1 + \frac{1}{x} - \frac{1}{x\pi(x)} \quad \text{(A3)}$$

From Eq. (13), it follows:

$$x\pi(x)(1 + \mu(x)) = 1 \quad \text{(A4)}$$

$$\frac{d\alpha}{dt}\frac{1}{\beta} = \frac{d\alpha}{dT} = \frac{dI}{dT}\exp(-I) = \frac{nE}{RT^2}(1+\mu(x))I\exp(-I) \quad \text{(A5)}$$

and

$$\Phi(m) = \frac{d\alpha}{dT}T^m = \frac{nE}{R}(1+\mu(x))I\exp(-I)T^{m-2} \quad \text{(A6)}$$

for dΦ/dT = 0:

$$\frac{nE}{R} I \exp(-I) T^{m-4} \cdot \left[\frac{d\mu(x)}{dT}T^2 + \frac{nE}{R}(1+\mu(x))^2(1-I) + (1+\mu(x))(m-2)T\right] = 0 \quad \text{(A7)}$$

$$\frac{d\mu(x)}{dT}T^2 = -\frac{d\mu(x)}{dx}\frac{E}{R} = -\frac{d(1/x\pi(x))}{dx}\frac{E}{R} \quad \text{(A8)}$$

$$\frac{d\mu(x)}{dT}T^2 = \frac{\pi(x) + x\pi'(x)}{x\pi^2(x)}T = (1 + \mu(x))(2 - x\mu(x))T \quad \text{(A9)}$$

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SAŽETAK

Položaj α = 0,632 u neizotermnoj JMA kinetici

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Johnson-Mehl-Avramijev matematički model brzine procesa nukleacije i rasta, $d\alpha/dT$, u neizotermnim uvjetima uporabljen je kao osnova za proučavanje funkcija oblika $\Phi(m) = (d\alpha/dT)T^m$, gdje je $m \in \Re$. Proučavanjem konverzije, α, procesa nukleacije i rasta pri temperaturi maksimuma funkcije $\Phi(m)$, $T = T(m)$, pokazano je da kada reducirana energija aktivacije, $x = E/RT$, teži u beskonačnost ($x \to \infty$), konverzija pri temperaturi koja odgovara maksimumu funkcije $\Phi(m)$, $\alpha(m)$, teži vrijednosti 0,632 za svaki m. Nadalje, pokazano je da, bez obzira na iznos reducirane energije aktivacije, konverzija procesa nukleacije i rasta iznosi 0,632 pri temperaturi maksimuma funkcije $\Phi(m)$ za određenu vrijednost parametra m iz intervala: $1 \le m \le 2$.