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SOME CRITICAL CONSIDERATIONS CONCERNING THE JMAYK EQUATION IN ISOTHERMAL AND NON-ISOTHERMAL CONDITIONS

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ABSTRACT

Some equations concerned with the formal theory of nuclei growth followed by ingestion and overlapping of nuclei are critically analysed. Some criticisms concerning the isothermal and non-isothermal forms of the JMAYK equation are also presented.

INTRODUCTION

The JMAYK (Johanson, Mehl, Avrami, Yerofeev, Kolmogorov) equation is used to describe physical changes such as glass crystallization, as well as heterogeneous chemical reactions such as solid–gas decompositions [1–7]. The isothermal form of the JMAYK equation is given as

$$-\ln(1-\alpha) = kt^r \qquad (1)$$

where α is the degree of conversion, t is time, k is the rate constant, and r is an exponent whose value is an integer which varies from 1 to 4.

Various aspects of the non-isothermal form of eqn. (1) have been summarized in an excellent article by Kemeny and Šesták [2].

The present work is concerned with some critical points regarding the possibility of obtaining an equation of the form of eqn. (1) from the formal theories of the kinetics of nucleation and growth of nuclei.

THE ISOTHERMAL JMAYK EQUATION

If growing nuclei ingest sites where nuclei could appear (potential nuclei), the ingested sites are considered as giving rise to "phantom" nuclei [3,8,9].

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In such conditions let N_0 be the number of potential nuclei in the system under investigation at $t = 0$. At time t, the system contains $N'(t)$ potential nuclei, $N(t)$ growing nuclei and $N''(t)$ potential nuclei which have been ingested by growing nuclei.

The conservation law of the total number of nuclei gives, successively

$$N + N' + N'' = N_0 \tag{2}$$

$$\mathrm{d}N + \mathrm{d}N' + \mathrm{d}N'' = 0 \tag{3}$$

Considering a one-step nucleation, it follows that

$$\mathrm{d}N = k_1 N' \,\mathrm{d}t = k_1(N_0 - N - N'')\,\mathrm{d}t \tag{4}$$

For negligible N'', the integral form of this equation is

$$N = N_0(1 - \mathrm{e}^{-k_1 t}) \tag{5}$$

From eqns. (2), (4) and (5),

$$N' = N_0\,\mathrm{e}^{-k_1 t} \tag{6}$$

and

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 k_1\,\mathrm{e}^{-k_1 t} \tag{7}$$

For the derivative of N'' with respect to α, we use the relationship

$$\frac{\mathrm{d}N''}{\mathrm{d}\alpha} = \frac{N'}{1 - \alpha} \tag{8}$$

Accepting that eqns. (3), (4) and (8) are valid we obtain

$$\mathrm{d}N' + k_1 N' \,\mathrm{d}t + \frac{N'}{1 - \alpha}\,\mathrm{d}\alpha = 0 \tag{9}$$

Dividing this by N' and integrating in the intervals $[o, t]$, $[o, \alpha]$, $[N_0, N']$ leads to

$$\ln\frac{N'}{N_0} - \ln(1 - \alpha) + k_1 t = 0 \tag{10}$$

and

$$N' = N_0\,\mathrm{e}^{-k_1 t}(1 - \alpha) \tag{11}$$

Taking into account relationship (4),

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 k_1\,\mathrm{e}^{-k_1 t}(1 - \alpha) \tag{12}$$

This equation is valid when N'' is not neglected, and consequently contains the supplementary factor $(1 - \alpha)$, as compared with eqn. (7).

Taking into account the general relationship [2,3,8,9]

$$V(t) = \int_0^t \sigma\left[\int_x^t G(y)\,\mathrm{d}y\right]^{\lambda}\left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_{t=x}\mathrm{d}x \tag{13}$$

(meanings of the symbols as given in the works quoted) and given that, by definition,

$$\alpha = \frac{V(t)}{V_0} \tag{14}$$

for three-dimensional growth of nuclei with a constant rate of growth ($G(x) = k_2$) and nucleation rate ($\mathrm{d}N/\mathrm{d}t$) given by eqns. (12) and (7) respectively, it turns out that

$$\alpha = \frac{\sigma N_0 k_1 k_2^3}{V_0} \int_0^t (t-x)^3 \, \mathrm{e}^{-k_1 x}(1-\alpha(x)) \, \mathrm{d}x \tag{15}$$

and

$$\alpha_{\mathrm{ex}} = \frac{\sigma N_0 k_1 k_2^3}{V_0} \int_0^t (t-x)^3 \, \mathrm{e}^{-k_1 x} \, \mathrm{d}x \tag{16}$$

where α_{ex} is the extended degree of conversion corresponding to the omission of the ingestion of the potential nuclei.

For the constant factors before the integrals from eqns. (15) and (16), we will use the following notation

$$k = \frac{\sigma N_0 k_1 k_2^3}{V_0} \tag{17}$$

Now let us show that there is no compatibility between relationships (15) and (16) and the known Avrami equations [1–3,5,8–9]

$$\left.\begin{aligned} \frac{\mathrm{d}\alpha}{\mathrm{d}\alpha_{\mathrm{ex}}} &= 1-\alpha \\ -\ln(1-\alpha) &= \alpha_{\mathrm{ex}} \end{aligned}\right\} \tag{18}$$

For the integrals from eqns. (15) and (16), which depend on the parameter t, the following theorem is valid [10–12].

Theorem

If in the function

$$F(t) = \int_{a(t)}^{b(t)} f(x, t) \, \mathrm{d}x \tag{19}$$

$f(x, t)$ and its partial derivative $f_t'(x, t)$ are continuous for $x \in [a, b]$ and $t \in [t_1, t_2]$, a, b, t_1 and t_2 being constants; and if $a(t)$ and $b(t)$ are continuous in the interval $[t_1, t_2]$, with continuous derivatives, and fulfil the condition $a \leqslant a(t) \leqslant b(t) \leqslant b$; then $F(t)$ is continuous and differentiable, its derivative being given by

$$F'(t) = \int_{a(t)}^{b(t)} f_t'(x, t) \, \mathrm{d}x + f(b(t), t) b'(t) - f(a(t), t) a'(t) \tag{20}$$

Taking into account eqn. (20), from eqn. (15) and by considering four successive derivatives with respect to t we obtain

$$\frac{d\alpha}{dt} = 3k\int_0^t (t-x)^2 \, e^{-k_1 x}(1-\alpha(x)) \, dx \tag{21}$$

$$\frac{d^2\alpha}{dt^2} = 6k\int_0^t (t-x) \, e^{-k_1 x}(1-\alpha(x)) \, dx \tag{22}$$

$$\frac{d^3\alpha}{dt^3} = 6k\int_0^t e^{-k_1 x}(1-\alpha(x)) \, dx \tag{23}$$

$$\frac{d^4\alpha}{dt^4} = 6k \, e^{-k_1 t}(1-\alpha) \tag{24}$$

Similarly, from eqn. (16), we obtain

$$\frac{d^4\alpha_{ex}}{dt^4} = 6k \, e^{-k_1 t} \tag{25}$$

Obviously, relationships (24) and (25) are by no means equivalent to relationship (18).

The search for an adequate relationship between α and α_{ex} using eqns. (24) and (25) is a fairly complicated problem which is not, in our opinion, worth considering. In such conditions, eqn. (24) can be considered independently of eqn. (25) as giving an adequate description of the phenomenon under investigation, i.e. introduction of α_{ex} does not help much.

Relationship (24) cannot be used directly, as it cannot be integrated. Some mathematical models could be of help here.

CRITICAL CONSIDERATIONS CONCERNING RELATIONSHIP (8)

We consider relationship (8) to be inadequate for the description of the ingestion of potential nuclei by growing nuclei. Two main objections can be noted.

Equation (8) does not fulfil the initial condition for $\alpha = 0$ (t = 0). Indeed, according to eqn. (8)

$$\left(\frac{dN''}{d\alpha}\right)_{\alpha=0} = N'(t=0) = N_0 \tag{26}$$

which is an incorrect result.

In our opinion, $(dN''/d\alpha)_{\alpha=0}$ and $(dN''/d\alpha)_{\alpha=1}$ should be equal to 0 (in the worst case, to a finite number). According to relationship (8),

$$\left(\frac{dN''}{d\alpha}\right)_{\alpha=1} = 0 \tag{27}$$

which is correct.

(2) Equation (8) does not contain any constant which depends on temperature as well as on the properties of the system under investigation. Taking this observation into account, eqn. (8) should be written as

$$\frac{dN''}{d\alpha} = k_3 \frac{N'}{1-\alpha} \tag{28}$$

From eqn. (3), taking into account eqns. (4) and (28), we obtain

$$N' = N_0\,e^{-k_1 t}(1-\alpha)^{k_3} \tag{29}$$

and

$$\frac{dN}{dt} = N_0 k_1\,e^{-k_1 t}(1-\alpha)^{k_3} \tag{30}$$

Introducing eqn. (30) into eqn. (13) and taking four successive derivatives with respect to t, it turns out that

$$\frac{d^4\alpha}{dt^4} = 6k\,e^{-k_1 t}(1-\alpha)^{k_3} \tag{31}$$

with the condition $k_3 < 1$, as

$$\left(\frac{dN''}{d\alpha}\right)_{\alpha=0} = k_3 N_0 < N_0 \tag{32}$$

Nevertheless, relationship (28) does not fulfil the boundary condition for $\alpha = 0$, and should therefore be used with care.

Another equation which can be considered instead of eqn. (8) is

$$\frac{dN''}{d\alpha} = k_4 N' h(\alpha) \tag{33}$$

where k_4 depends on temperature, and $h(\alpha)$ is a function which takes into account the ingestion and is compatible with the boundary conditions

$$\left(\frac{dN''}{d\alpha}\right)_{\alpha=0} = \left(\frac{dN''}{d\alpha}\right)_{\alpha=1} = 0 \tag{34}$$

Introducing relationships (4) and (33) into eqn. (3), it turns out that

$$N' = N_0\,e^{-k_1 t}\,e^{-k_4 \int_0^\alpha h(\alpha)\,d\alpha} \tag{35}$$

and

$$\frac{dN}{dt} = N_0 k_l\,e^{-k_1 t}\,e^{-k_4 \int_0^\alpha h(\alpha)\,d\alpha} \tag{36}$$

Introducing eqn. (36) into eqn. (13), and taking four successive derivatives with respect to t, we obtain

$$\frac{d^4\alpha}{dt^4} = 6k\,e^{-k_1 t}\,e^{-k_4 \int_0^\alpha h(\alpha)\,d\alpha} \tag{37}$$

Let us consider three possible forms of $h(\alpha)$, and the corresponding particular forms of eqn. (37).

$$h_1(\alpha) = \alpha(1 - \alpha) \tag{38}$$

$$\frac{d^4\alpha}{dt^4} = 6k\ e^{-k_1 t}\ e^{-k_4\alpha^2((3-2\alpha)/6)} \tag{39}$$

$$h_2(\alpha) = \frac{\alpha}{1 - \alpha} \tag{40}$$

$$\frac{d^4\alpha}{dt^4} = 6k\ e^{-k_1 t}\ e^{k_4\alpha}(1 - \alpha)^{k_4} \tag{41}$$

$$h_3(\alpha) = \alpha$$

$$\frac{d^4\alpha}{dt^4} = 6k\ e^{-k_1 t}\ e^{-k_4\alpha^2} \tag{42}$$

Another possibility (limited by mathematical difficulties) consists in replacing eqn. (8) with an equation which contains dN''/dt,

$$\frac{dN''}{dt} = k_5 N' q(\alpha) \tag{43}$$

where k_5 is dependent on temperature.

Introducing eqns. (43) and (4) into eqn. (3), and performing some simple calculations, we obtain

$$N' = N_0\ e^{-k_1 t}\ e^{-\int_0^t k_5 q(\alpha)\ dt} \tag{44}$$

$$\frac{dN}{dt} = N_0 k_1\ e^{-k_1 t}\ e^{-\int_0^t k_5 q(\alpha)\ dt} \tag{45}$$

The problem, which is unsolvable for the moment, consists in the integral $\int_0^t k_5 q(\alpha)\ dt$, which cannot be used directly in calculations. Nevertheless, introducing eqn. (45) into eqn. (13), and taking successively the first four derivatives with respect to t, it turns out that

$$\frac{d^4\alpha}{dt^4} = 6k\ e^{-k_1 t}\ e^{\int_0^t k_5 q(\alpha)\ dt} \tag{46}$$

Another possibility consists in replacing eqn. (8) with the equation

$$\frac{dN''}{dt} = k_6 N' N \tag{47}$$

where k_6 depends on temperature. Equation (47) adequately describes the law of ingestion of potential nuclei by growing nuclei, as (1) it fulfils the boundary conditions and (2) it fulfils the requirement that dN''/dt be proportional to the number of potential nuclei N' as well as to the number of growing nuclei N.

Introducing in eqn. (47) the number N from eqn. (2), according to the relationship

$$N = N_0 - N' - N'' \tag{48}$$

we obtain

$$\frac{\mathrm{d}N''}{\mathrm{d}t} = k_6 N'(N_0 - N' - N'') \tag{49}$$

Introducing eqns. (49) and (4) into eqn. (3), we obtain a relationship which cannot be integrated directly, owing to N''. To overcome this difficulty, in a first approximation (zero order approximation), we shall consider that $N'' \ll N_0 - N'$. Under these conditions, eqn. (49) turns into

$$\frac{\mathrm{d}N''}{\mathrm{d}t} = k_6 N'(N_0 - N') \tag{50}$$

For $N'' \approx 0$, relationships (5) and (6) are valid, thus

$$\frac{\mathrm{d}N''}{\mathrm{d}t} = k_6 N' N_0 (1 - \mathrm{e}^{-k_1 t}) \tag{51}$$

Under these conditions, eqn. (3) turns into

$$\frac{\mathrm{d}N'}{N'} + k_1\ \mathrm{d}t + k_6 N_0 (1 - \mathrm{e}^{-k_1 t})\ \mathrm{d}t = 0 \tag{52}$$

By integrating and performing the detailed calculations necessary, we obtain

$$N' = N_0\ \mathrm{e}^{-k_1 t}\ \mathrm{e}^{-N_0 k_6 (-(1/k_1) + t + (\mathrm{e}^{-k_1 t}/k_1))} \tag{53}$$

and

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 k_1\ \mathrm{e}^{-k_1 t}\ \mathrm{e}^{-N_0 k_6 / k_1 (\mathrm{e}^{-k_1 t} + k_1 t - 1)} \tag{54}$$

Introducing this result into (13), and taking into account eqn. (14), it turns out that

$$\alpha = k \int_0^t (t - x)^3\ \mathrm{e}^{-k_1 x}\ \mathrm{e}^{-N_0 (k_6 / k_1)(\mathrm{e}^{-k_1 x} + k_1 x - 1)}\ \mathrm{d}x \tag{55}$$

Taking successively the first four derivatives with respect to t in eqn. (55), we obtain

$$\frac{\mathrm{d}^4 \alpha}{\mathrm{d}t^4} = 6k\ \mathrm{e}^{-k_1 t}\ \mathrm{e}^{-N_0 (k_6 / k_1)(\mathrm{e}^{-k_1 t} + k_1 t - 1)} \tag{56}$$

These critical considerations regarding eqn. (8) and possible substitutions lead us to conclude that improvements are needed in the formal theory of nuclei growth with ingestion and mutual overlapping.

Some earlier criticisms concerning eqn. (18) and its approximate nature are presented in a comprehensive monograph by Rozovskii [13].

From eqn. (4) for $N''=0$ accepted as Postulated Primary Isothermal Differential Kinetic Equation (P-PIDKE) [14,15], using

$$T=\theta(t) \tag{57}$$

and operating a classical non-isothermal change (CNC) with some elementary calculations, we obtain

$$N=N_0\left(1-e^{-\int_0^t k_1(\theta(t'))\,dt'}\right) \tag{58}$$

For the ingestion case we have to introduce eqns. (4) and (28) accepted as P-PIDKE in eqn. (3). It then turns out that

$$\frac{dN'}{N'}+k_1(\theta(t))\,dt+\frac{k_3(\theta(t))}{1-\alpha}\,d\alpha=0 \tag{59}$$

After performing the CNC and integration, we obtain

$$N'=N_0\,e^{-\int_0^t k_1(\theta(t'))\,dt'}\,e^{-\int_0^\alpha (k_3(\theta(t))/1-\alpha)\,d\alpha} \tag{60}$$

For absence of ingestion,

$$\frac{dN}{dt}=N_0\,e^{-\int_0^t k_1(\theta(t'))\,dt'}k_1(\theta(t)) \tag{60a}$$

and

$$\alpha_{ex}=\frac{\sigma N_0}{V_0}\int_0^t\left[\int_x^t k_2(\theta(y))\,dy\right]^3 k_1(\theta(x))\,e^{-\int_0^x k_1(\theta(t'))\,dt'}\,dx \tag{60b}$$

For the general case, eqn. (4) taking into account eqn. (60) takes the form

$$\frac{dN}{dt}=N_0k_1(\theta(t))\,e^{-\int_0^t k_1(\theta(t'))\,dt'}\,e^{-\int_0^\alpha (k_2(\theta(t))/1-\alpha)\,d\alpha} \tag{61}$$

The problems raised by the integral $\int_0^\alpha (k_2(\theta(t))/1-\alpha)\,d\alpha$ could be solved eventually by writing it in the form

$$\int_0^\alpha \frac{k_2(\theta(t))}{1-\alpha}\,d\alpha=\int_0^{\alpha(t)}\frac{k_2(\theta(t'))}{1-\alpha(t')}\frac{d\alpha}{dt}(t')\,dt' \tag{62}$$

For non-isothermal conditions, taking into account that in eqn. (13) $G(y)$ can be temperature dependent,

$$\alpha=\frac{\tau N_0}{V_0}\int_0^t\left[\int_x^t k_2(\theta(y))\,dy\right]^3 k_1(\theta(x))$$
$$\times\, e^{-\int_0^x k_1(\theta(t'))\,dt'}\,e^{-\int_0^{\alpha(x)}(k_2(\theta(t))/1-\alpha)\,d\alpha}\,dx \tag{63}$$

With eqn. (63) we cannot take successive derivatives with respect to t in order to get rid of the integral, as $k_2(\theta(t))$ depends on temperature at time t. The mathematical difficulties raised by the non-isothermal JMAYK equation are obvious.

The use of an equation of the form of eqn. (33) leads to the same type of integral

$$I_1 = \int_0^{\alpha} k_4(\theta(t))h(\alpha)\,\mathrm{d}\alpha \tag{64}$$

which is, for the moment, unsolvable.

Using an equation of the form of eqn. (43) as P-PIDKE leads after some calculations to

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 k_1(\theta(t))\,\mathrm{e}^{-\int_0^t k_1(\theta(t'))\,\mathrm{d}t'}\,\mathrm{e}^{-\int_0^t k_5(\theta(t'))q(\alpha(t'))\,\mathrm{d}t'} \tag{65}$$

Thus

$$\alpha = \frac{\sigma N_0}{V_0}\int_0^t\left[\int_x^t k_2(\theta(y))\,\mathrm{d}y\right]^3 k_1(\theta(x))$$

$$\times\,\mathrm{e}^{-\int_0^x k_1(\theta(t'))\,\mathrm{d}t'}\,\mathrm{e}^{-\int_0^x k_5(\theta(t'))q(\alpha(t'))\,\mathrm{d}t'}\,\mathrm{d}x \tag{66}$$

Relationship (66) cannot be used either because of the mathematical complications which arise when trying to apply it.

Finally, let us consider accepting eqn. (47) as P-PIDKE. In a first approximation (zero order approximation), by neglecting N'', we obtain

$$\frac{\mathrm{d}N''}{\mathrm{d}t} = k_6(\theta(t))N'N_0\left(1 - \mathrm{e}^{-\int_0^t k_1(\theta(t'))\,\mathrm{d}t'}\right) \tag{67}$$

Introducing this result into eqn. (3), it turns out that

$$\frac{\mathrm{d}N'}{N'} + k_1(\theta(t))\,\mathrm{d}t + N_0 k_6(\theta(t))\left(1 - \mathrm{e}^{-\int_0^t k_1(\theta(t'))\,\mathrm{d}t'}\right)\mathrm{d}t = 0 \tag{68}$$

Integration of eqn. (68) leads to

$$N' = N_0\,\mathrm{e}^{-\int_0^t k_1(\theta(t'))\,\mathrm{d}t'}\,\mathrm{e}^{-N_0\int_0^t k_6(\theta(t_2))(1-\exp[-\int_0^{t_2} k_1(\theta(t_1))\,\mathrm{d}t_1])\,\mathrm{d}t_2} \tag{69}$$

From this result and relationships (4), (13) and (14), we obtain

$$\alpha = \frac{\tau N_0}{V_0}\int_0^t\left[\int_\alpha^t k_2(\theta(y))\,\mathrm{d}y\right]^3 k_1(\theta(x))$$

$$\times\,\mathrm{e}^{-\int_0^\alpha k_1(\theta(t'))\,\mathrm{d}t'}\,\mathrm{e}^{-N_0\int_0^\alpha k_6(\theta(t_2))(1-\exp[-\int_0^{t_2} k_1(\theta(t_1))\,\mathrm{d}t_1])\,\mathrm{d}t_2}\,\mathrm{d}x \tag{70}$$

which cannot be applied practically because of the mathematical difficulties.

By comparing α_{ex} given by eqn. (60b) with α given by eqns. (63), (66) or (70), we come to the conclusion that relationship (18) is not valid in non-isothermal conditions.

CONCLUSIONS

Some critical considerations concerning the JMAYK equation have been presented. It has been shown that the theory of nuclei growth is incompatible with the Avrami equation (eqn. (18)). A critical analysis of relationship (8), as well as of possible improvements to this relationship, were also presented. The mathematical difficulties associated with the non-isothermal JMAYK equation have been emphasized.

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