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Comparing the Johnson–Mehl–Avrami–Kolmogorov equations for isothermal and linear heating conditions

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Abstract

We present a derivation of the linear heating Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation for a constant nucleation rate and diffusion-controlled growth, in the hard impingement approximation. The result is compared with the linear heating JMAK equation for interface-controlled growth, and with the isothermal JMAK equation. We show that all approximations made in deriving the JMAK equations (i.e. including previous work) hold when the activation energies involved are large compared to the thermal energy, which turns out to be virtually always the case. Finally, we demonstrate in a simple way that within the JMAK framework, peak shift methods such as Kissinger analysis, Marseglia and Ozawa plots are formally equivalent and may all be used to analyse experimental data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Johnson–Mehl–Avrami–Kolmogorov (JMAK) transformation kinetics describes the extent to which a material is transformed during a certain phase transformation, as a function of temperature and time. This information is contained in the JMAK parameters, which are constant with respect to time and temperature. Crystallisation of amorphous materials and other solid state phase transformations are examples of transformations that are described by JMAK kinetics. The equations that describe the JMAK kinetics were first derived for transformations under isothermal annealing conditions [1–10]. Efforts have also been made to derive the JMAK equations under linear heating conditions [11–14]. The main interest for the linear heating JMAK equations lies in the fact that linear heating experiments are much faster than isothermal experiments, so that it takes less time to determine the JMAK parameters from a linear heating experiment. Also, isothermal experiments have the drawback that the sample needs to be heated to the desired temperature in a time that is much smaller than the transformation time. However, it is not obvious how the parameters determined from isothermal and linear heating experiments are related. Here, we shall try to clarify this problem, following a rather formal approach. The approach is more general than that of Vázquez et al. [14] as we do not assume that the

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progress of the transformation is determined by the number of atomic jumps.

We shall start from the equation that gives the volume fraction of the transformed material, x, as a function of time, t, for transformations controlled by nucleation and growth [1–9]

$$x(t) = 1 - \exp[-x_e(t)], \tag{1a}$$

with

$$x_e(t) = \int_0^t v(t,\tau)I(\tau)\,d\tau, \tag{1b}$$

where $v(t,\tau)$ is the volume of a particle of the product phase, nucleated at time τ, as a function of time and $I(t)$ is the nucleation rate at time t. Eq. (1a) accounts for the interaction between the particles in the latter stages of the transformation: nuclei are formed only in untransformed material and the particles will eventually impinge. The factor x_e is the ratio of the extended volume (see [9] for a comprehensive explanation) of the transformed material to the real volume of the system. Assuming isotropic growth in b dimensions (i.e. $b = 1$ when the nuclei grow out to a needle-like shape, $b = 2$ when they look like discs and $b = 3$ for spherically shaped particles of the product phase), the nuclei formed at time τ will have a volume

$$v(t,\tau) = g[R(t,\tau)]^b, \tag{2}$$

where g is a geometrical constant of order unity and R the radius of the particle. When the growth rate of the particle is $G(t)$, its radius will increase as

$$R(t,\tau) = \int_\tau^t G(\theta)\,d\theta, \tag{3}$$

where θ is a dummy parameter of dimension time, that runs from τ to t. Now, for any particular case of nucleation and growth, Eqs. (1b)–(3) can be evaluated along a temperature–time path of interest. In the next paragraph, we shall state the results for isothermal conditions.

2. The isothermal JMAK equations

We will first present the results of the derivation of the isothermal JMAK equation. This allows us to introduce the parameters and concepts that are characteristic to JMAK kinetics in the context of the more familiar isothermal JMAK equations and to point out exactly where the differences between isothermal and linear heating kinetics lie.

2.1. The isothermal JMAK equation

The volume fraction of the transformed material as a function of time during isothermal annealing is given by [9]

$$x(t) = 1 - \exp(-kt^n), \tag{4a}$$

with

$$k(T) = k_0 \exp\left(-\frac{\Delta H}{k_B T}\right). \tag{4b}$$

These equations are known as the isothermal JMAK equations. n, ΔH and k_0 are the JMAK parameters, which will be discussed in more detail below. k_B is the Boltzmann constant. Eqs. (4a) and (4b) have been derived from Eqs. (1a)–(3) for a number of special cases [10]: site saturated nucleation, a constant nucleation rate, an increasing/decreasing nucleation rate and for interface- and diffusion-controlled growth, assuming that the nucleation rate, $I(T)$, and the growth rate, $G(T)$, have an Arrhenian temperature dependence:

$$I(T) = I_0 \exp\left(-\frac{E_n}{k_B T}\right) \tag{5a}$$

and

$$G(T) = G_0 \exp\left(-\frac{E_g}{k_B T}\right). \tag{5b}$$

E_n and E_g are the activation energies for nucleation and growth, respectively, and I_0 and G_0 are constants with respect to temperature.

The exponential factors in Eqs. (5a) and (5b) are Boltzmann factors. They correspond to the fraction of atoms that have a thermal energy in excess of E_n or E_g, respectively. In Boltzmann statistics, these activation energies generally are a function of temperature, but are essentially constant at relatively low temperatures, i.e. when

$$E_n \gg k_B T \tag{6a}$$

and

$$E_g \gg k_B T. \tag{6b}$$

These inequalities are of crucial importance in JMAK kinetics. For isothermal kinetics they are implicitly assumed to hold by taking the temperature dependences of the nucleation and growth rates to be Arrhenian.

Combining the cases considered, the JMAK parameters can be expressed in terms of the nucleation and growth parameters [10].

For the Avrami exponent, n, we have

$$n = a + bc, \tag{7}$$

where a is the nucleation index ($a = 0$ for zero nucleation rate, $0 < a < 1$ for a decreasing nucleation rate, $a = 1$ for a constant nucleation rate and $a > 1$ when the nucleation rate increases as a function of time), b is the dimensionality of the growth and c is the growth index ($c = 1$ for interface-controlled growth and $c = 0.5$ when growth is diffusion-controlled). For the effective activation energy, we have

$$\Delta H = aE_{\mathrm{n}} + bcE_{\mathrm{g}}. \tag{8}$$

From Eqs. (7) and (8) we see that $\Delta H/n$, the parameter obtained from Kissinger analysis (see Section 4.1) is equal to the average of E_{n} and E_{g}, weighted by a and bc, respectively.

The expression for k_0 is

$$k_0 = \frac{g}{n} I_0^a G_0^{bc}, \tag{9}$$

where g is the geometrical constant of Eq. (2). Eq. (9) is not valid for $a = 0$; when the nucleation rate is zero, I_0^a should then be replaced with N, the (fixed) number of nuclei per unit volume.

It is emphasised that Eqs. (7)–(9) are nothing but a concise way of presenting the relationships between the JMAK parameters and the nucleation and growth parameters for the handful of special modes of nucleation and growth mentioned above. Of course, the JMAK parameters will always be related to the nucleation and growth parameters, but not necessarily through Eqs. (7)–(9).

It is also important to realise that the fact that JMAK kinetics are a convolution of nucleation and growth kinetics means that we cannot, in principle, obtain any information about the individual nucleation and growth processes from the JMAK parameters alone.

2.2. The isothermal JMAK rate equation

Having found the fraction transformed as a function of time, we can calculate the isothermal transformation rate equation by differentiating Eq. (4a) with respect to time:

$$\frac{\mathrm{d}x}{\mathrm{d}t}(t) = nkt^{n-1}\exp(-kt^n). \tag{10}$$

Eliminating the explicit time dependence of Eq. (10) by using Eq. (4a), we have

$$\frac{\mathrm{d}x}{\mathrm{d}t}(x) = nk^{1/n}(1-x)(-\ln(1-x))^{(n-1)/n}. \tag{11}$$

Eq. (11) is called the isothermal JMAK transformation rate equation.

3. The linear heating JMAK equation

Eqs. (1b)–(3) have been evaluated under linear heating conditions for a number of nucleation and growth mechanisms [11]. These are: site-saturated nucleation, zero nucleation rate or a constant nucleation rate (i.e. a nucleation rate that only has an implicit time dependence through T) and for interface-controlled growth. In this section, we shall first review the results for diffusion-controlled growth and then derive the linear heating JMAK equations for interface-controlled growth.

3.1. The result for interface-controlled growth

The linear heating JMAK equation for interface-controlled growth can be written as

$$x(t) = 1 - \exp(-k't^{2n}), \tag{12a}$$

with

$$k'(\beta, T) = k_0'\beta^n \exp\left(-\frac{\Delta H}{k_{\mathrm{B}}T}\right), \tag{12b}$$

where β is the heating rate, $T = \beta t$, and n and ΔH are given by Eqs. (7) and (8) for $c = 1$, i.e. for interface-controlled growth. The expression for k_0' is shown to be [11]

$$k_0' = gI_0^a G_0^{bc} C_1 \left(\frac{k_{\mathrm{B}}}{E_{\mathrm{g}}}\right)^{1+bc}, \tag{13}$$

which, like Eq. (9), is also not valid for $a = 0$. C_1 is a constant of order unity, to be discussed in detail in Section 3.1.

Comparing the isothermal and the linear heating JMAK equations, we see that

1. the Avrami exponents differ by a factor two;
2. the rate factor, $k'(\beta, T)$, in Eq. (12b) implicitly depends on time through $T = \beta t$, and explicitly depends on the heating rate through the β^n term.

Apart from implicitly assuming that Eqs. (6a) and (6b) hold by using Eqs. (5a) and (5b) for the nucleation and growth rate, Eqs. (6a) and (6b) are used explicitly as an approximation in the derivation of Eqs. (12a) and (12b). As this puts a lot of importance on Eqs. (6a) and (6b), we shall investigate how restrictive they are. Obviously, the inequalities will always be satisfied at the early stages of a linear heating experiment and will always be violated if we wait long enough. However, Eqs. (12a) and (12b) will essentially be correct during the *entire* transformation when

$$t_\mathrm{f} \ll \frac{E_\mathrm{n}}{k_\mathrm{B}\beta} \tag{14a}$$

and

$$t_\mathrm{f} \ll \frac{E_\mathrm{g}}{k_\mathrm{B}\beta}, \tag{14b}$$

where t_f is the time at which the transformation is effectively completed. Eqs. (14a) and (14b) are, to a certain extent, self-fulfilling: if the activation energies for nucleation and growth are small, nucleation and growth are fast, resulting in a small t_f. As this does not tell us how restrictive Eqs. (14a) and (14b) are, we need to express t_f in terms of the JMAK parameters.

Let us say that the transformation is over when $x_\mathrm{e}(t_\mathrm{f}) = 5$ (i.e. when $x(t_\mathrm{f}) = 1 - \mathrm{e}^{-5} = 0.99$). From Eqs. (1a), (12a) and (12b), we see that this is equivalent to saying

$$k'_0\beta^n \exp\left(-\frac{\Delta H}{k_\mathrm{B}\beta t_\mathrm{f}}\right)t_\mathrm{f}^{2n} = 5. \tag{15}$$

As both the terms in Eq. (15) that depend on t_f are *increasing* functions of t_f, we may substitute the inequalities (14a) and (14b) into Eq. (15) and get

$$k'_0\left(\frac{E_\mathrm{n,g}}{k_\mathrm{B}}\right)^{2n} \gg 5\beta^n \exp\left(\frac{\Delta H}{E_\mathrm{n,g}}\right). \tag{16}$$

As long as ΔH is of the same order of magnitude as the activation energies of nucleation and growth, the right hand side of the inequality is of the order of 10–10^3, as experimental heating rates are of the order of 1 K/s and the Avrami exponent lies in the range 0.5–4.5 [9]. For the transformation to be slow at room temperature, we must have $E_\mathrm{n,g} \gg k_\mathrm{B}T_\mathrm{R}$, so that the second term on the left hand side is of the order 10^{12} or larger. As k'_0 is usually large too, the inequality is satisfied.

When ΔH is one or two orders of magnitude larger than the activation energy for either nucleation or growth, Eq. (16) can be violated. Physically, this means that Eqs. (12) are not valid when the transformation is strongly dominated by either nucleation or growth. Such cases, however, are not in the spirit of the JMAK model and it has recently been shown that the *isothermal* JMAK equation is also not valid when the transformation is dominated by growth [15].

3.2. Derivation for interface-controlled growth

In his derivation [11], Woldt uses the exponential integral function to evaluate Eqs. (1b) and (3) under linear heating conditions. This approach is mathematically rather laborious. In the next section, we outline a simpler approach and show that both approaches yield the same result. Essentially, we use Eqs. (6a) and (6b) as an approximation earlier than Woldt does.

Let us consider the special case of a constant nucleation rate and interface-controlled growth, with the nucleation and growth rates given by Eqs. (5a) and (5b). Eq. (3) then becomes

$$R(t,\tau) = G_0\int_\tau^t \exp\left(-\frac{1}{\alpha\theta}\right)\mathrm{d}\theta, \tag{17}$$

where we have defined $\alpha \equiv k_\mathrm{B}\beta/E_\mathrm{g}$. Substituting $\xi = 1/\theta$, we have

$$R(t,\tau) = -G_0\int_{1/\tau}^{1/t} \xi^{-2}\exp\left(-\frac{\xi}{\alpha}\right)\mathrm{d}\xi. \tag{18}$$

Now, if we assume that, as ξ runs from $1/\tau$ to $1/t$, the $\exp(-\xi/\alpha)$ term varies much more quickly than the ξ^{-2} term, we have

$$R(t,\tau) \approx -G_0\xi^{-2}\int_{1/\tau}^{1/t}\exp\left(-\frac{\xi}{\alpha}\right)\mathrm{d}\xi$$
$$= \left(\frac{G_0}{\alpha}\right)^c [f(t) - f(\tau)]^c$$

with $c = 1$, where we have written for convenience

$$f(t) \equiv (\alpha t)^2 \exp\left(-\frac{1}{\alpha t}\right). \tag{20}$$

Putting Eqs. (2) and (19) into (1b) gives

$$x_{\mathrm{e}}(t) = \frac{C_0}{\alpha^{bc}} \int_0^t [f(t) - f(\tau)]^{bc} \exp\left(-\frac{\varepsilon}{\alpha\tau}\right) \mathrm{d}\tau, \tag{21}$$

where we have defined $C_0 \equiv gI_0G_0^{bc}$ and $\epsilon \equiv E_{\mathrm{n}}/E_{\mathrm{g}}$.

The power term in Eq. (21) can be expanded as a binomial series and the integral evaluated analytically. This is done in Appendix A and gives

$$x_{\mathrm{e}}(t) = k_0'\beta^{1+bc}t^{2(1+bc)} \exp\left(-\frac{E_{\mathrm{n}} + bcE_{\mathrm{g}}}{k_{\mathrm{B}}\beta t}\right), \tag{22}$$

where k_0' is given by Eq. (13) with C_1 (also found in Eq. (13)) shown to be equal to

$$C_1(bc, \varepsilon) = \sum_{j=0}^{\infty} \binom{bc}{j} \frac{(-1)^j}{j + \varepsilon}. \tag{23}$$

Putting Eq. (22) back into Eq. (1a) and using Eqs. (7)–(9) finally leads to Eqs. (12a) and (12b) for $a = 1$ and $c = 1$, completing the derivation.

Eq. (23) is beautifully concise and gives the most general expression for C_1, but it does not give much physical insight in how C_1 depends on bc and ε. For the cases considered, i.e. one, two or three-dimensional interface-controlled growth, bc can take the values 1, 2 or 3. For integer values of bc, the series terminates when $j = bc$; the binomial coefficients are then equal to zero when $j > bc$. Evaluating the summation, we find

$$C_1(1, \varepsilon) = \frac{1}{\varepsilon + \varepsilon^2}, \tag{24a}$$

$$C_1(2, \varepsilon) = \frac{2}{2\varepsilon + 3\varepsilon^2 + \varepsilon^3}, \tag{24b}$$

$$C_1(3, \varepsilon) = \frac{6}{6\varepsilon + 11\varepsilon^2 + 6\varepsilon^3 + \varepsilon^4}. \tag{24c}$$

Eqs. (24a) and (24c) show that C_1 is a smooth, decreasing function of ε ($=E_{\mathrm{n}}/E_{\mathrm{g}}$) and that it is of the order unity when ϵ ranges from 0.5 to 2. Note that $C(bc, 1) = (1 + bc)^{-1}$.

Eqs. (22) and (24) are identical to Woldt's result. This implies that the approximations we made in deriving Eqs. (19) and (22) are valid as long as Eqs. (6a) and (6b) hold.

3.3. Derivation for diffusion-controlled growth

When growth of the particles is controlled by diffusion, their growth rate is equal to

$$G(t) = \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{D}{R}, \tag{25}$$

provided the diffusion constant, D, does not change during the transformation and depends on temperature through

$$D(T) = D_0 \exp\left(-\frac{E_{\mathrm{d}}}{k_{\mathrm{B}}T}\right). \tag{26}$$

Substituting Eq. (26) into Eq. (25) and separating the variables gives

$$\int_0^R R'\,\mathrm{d}R' = \frac{1}{2}R^2 = D_0 \int_\tau^t \exp\left(-\frac{1}{\alpha\theta}\right) \mathrm{d}\theta, \tag{27}$$

where we have defined $\alpha \equiv k_{\mathrm{B}}\beta/E_{\mathrm{d}}$. Using the same approximation as we used when deriving Eq. (19), we can evaluate the integral on the right hand side of Eq. (27) to obtain

$$R(t, \tau) = \left(\frac{2D_0}{\alpha}\right)^c [f(t) - f(\tau)]^c, \tag{28}$$

where $c = 0.5$. The rest of the derivation is now analogous to the derivation for interface-controlled growth, presented in the previous section; see Eq. (19) and following. This finally leads to Eq. (22) with $c = 0.5$, $E_{\mathrm{g}} = E_{\mathrm{d}}$ and k_0' given by Eq. (13) with G_0 replaced by $2D_0$; C_1 in Eq. (13) is again given by Eq. (23). However, as we now have $c = 0.5$, bc can take the non-integer values $bc = 0.5$ and 1.5, for which the series in Eq. (23) does not terminate. Fortunately, it converges very quickly. Fig. 1 shows that taking the first five terms in Eq. (23) gives values for $C_1(0.5, \varepsilon)$ and $C_1(1.5, \varepsilon)$ that compare very well with solutions obtained by numerically solving the integral in Eq. (21) for $bc = 0.5$ and 1.5.

This completes our derivation of Eqs. (12a) and (12b) for diffusion-controlled growth.

3.4. The linear heating JMAK rate equation

As for the isothermal case (see Section 2 B), we can calculate the linear heating JMAK transformation rate equation by differentiating Eqs. (12a) and (12b) with

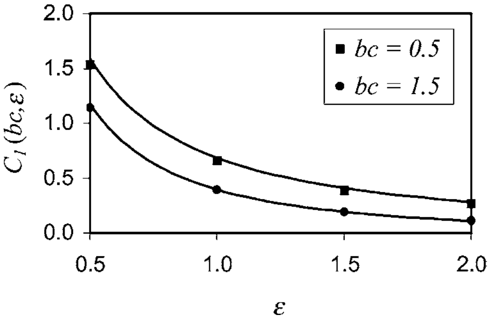

Fig. 1. Plot of C_1 from Eq. (13) vs. $\varepsilon = E_n/E_g$, the ratio of the activation energies for nucleation and growth, for two non-integer values of bc. Squares: numerical solutions of $C_1(0.5, \varepsilon)$. Dots: numerical solutions of $C_1(1.5, \varepsilon)$. Full lines: plots of $C_1(bc, \varepsilon)$ for the corresponding values of bc, obtained by truncating Eq. (23) after the fifth term.

respect to time. In the limit $\Delta H/2n \gg k_B T$ (which is hardly restrictive, as we already have $E_n \gg k_B T$ and $E_g \gg k_B T$), we then find that

$$\frac{dx}{dt}(x) = \frac{\Delta H}{k_B \varphi}(k')^{1/n}(1-x)(-\ln(1-x))^{(n-1)/n}. \tag{29}$$

We now see that, unlike $x(t)$, dx/dt has the same form for both the isothermal and the linear heating case, apart from the different pre-factors: $nk_0^{1/n}$ for Eq. (11) and $(k'_0)^{1/n}\Delta H/k_B$ for Eq. (29) (note that the heating rate drops out) and for the fact that Eq. (29) has an implicit time dependence through the temperature dependence of the rate factor, Eq. (12b). Eq. (29) is a very important result; there has been a lot of speculation in the literature on the correct form of the non-isothermal transformation rate equation. Eq. (11) is often assumed to be valid for any temperature–time path; this is *not* generally correct as Eq. (11) is obtained from the *isothermal* JMAK equation. Henderson has argued that "*if it can be shown that the transformation rate depends only on the state variables of fraction transformed and temperature, and not on the thermal history*" [12], then Eq. (11) is also valid for non-isothermal transformations. In a latter article [13], Henderson argues that, in general, the transformation rate *does* depend on the thermal history, and that Eq. (11) is only valid for non-isothermal reactions for certain special cases, namely site-saturated nucleation, a zero nucleation rate and isokinetic transformations (i.e. transformation for which $E_n = E_g$). It thus follows that Eqs. (11) and (29) should both describe the transformation rate under linear heating conditions, when $\varepsilon = E_n/E_g = 1$. Therefore, the pre-factors of Eqs. (11) and (29) should be the same. We shall verify that this is indeed so, taking a constant nucleation rate ($a = 1$) as an example.

The ratio, ρ, of the pre-factors is in that case

$$\rho = \frac{\Delta H}{nk_B}\left(\frac{k'_0}{k_0}\right)^{1/n}. \tag{30}$$

This ratio should be equal to one for $E_n = E_g = \Delta H/n$. With Eqs. (9) and (13), this gives

$$\rho = \frac{\Delta H}{nk_B}(nC_1(bc,1))^{1/n}\left(\frac{nk_B}{\Delta H}\right)^{(1+bc)/n}, \tag{31}$$

which is indeed equal to one, as $C_1(bc,1) = (1+bc)^{-1} = n^{-1}$ for the case considered. Because of the remarkable consistency between the two approaches, we may feel confident that they are both correct. However, this only justifies the use of Eq. (11) for *linear heating* conditions. There may well be non-isothermal conditions for which Eq. (11) does not hold. Whether it does or not may be checked by integrating Eqs. (1a) and (3) for the temperature–time path in question.

The fact that Eqs. (11) and (29) are proportional means that under linear heating conditions the transformation rate is indeed independent on thermal history.

4. Determining the linear heating parameters

Now that we have shown that Eq. (11) is proportional to Eq. (29), we may use the methods outlined by Henderson [12] to obtain the JMAK parameters. However, there are a few reasons why we would like to derive these methods here. Firstly, their derivation becomes much simpler now that we have derived Eqs. (12a) and (12b), in addition to Eq. (29). Secondly, we wish to point out that the derivations are valid as long as Eqs. (6a) and (6b) hold and that no additional assumptions need to be made. Thirdly, we found that one of our results contradicts Henderson's.

4.1. Peak shift methods: $\Delta H/n$

During the transformation, after most of the nuclei have formed and the particles grow, the transformation rate goes through a maximum, before impingement of the particles of the transformed phase brings the process to an end. This peak in $\mathrm{d}x/\mathrm{d}t$ occurs when $\mathrm{d}^2x/\mathrm{d}t^2 = 0$. The temperature at which this peak occurs is denoted T_p. Taking the second derivative of Eqs. (12a) and (12b) with respect to time and setting it to zero gives

$$\left(\frac{\Delta H}{k_\mathrm{B}T_\mathrm{p}} + 2n - 2\right) = \left(\frac{\Delta H}{k_\mathrm{B}T_\mathrm{p}} + 2n\right)x_\mathrm{e}(T_\mathrm{p}). \tag{32}$$

Assuming, as before, that $\Delta H/2n \gg k_\mathrm{B}T$, we see that

$$x_\mathrm{e}(T_\mathrm{p}) \approx 1. \tag{33}$$

This means that under linear heating conditions, the extended volume is equal to the real volume of the system at the peak in the transformation rate. This is mostly a numerical coincidence, a consequence of Eqs. (6a) and (6b); from Eqs. (4a) and (4b), it can easily be shown that under isothermal conditions, we have $x_\mathrm{e}(T_\mathrm{p}) = (n-1)/n$. Nonetheless, $x_\mathrm{e} = 1$ has some physical significance, as, during the transformation, the transformation rate is decreased by impingement and impingement becomes important when the extended volume approaches the real volume.

The true importance of Eq. (33) lies in the fact that the fraction transformed at the peak in the transformation rate is equal to $x(T_\mathrm{p}) = 1 - \mathrm{e}^{-1} = 0.63$, *regardless of the heating rate*. This fact lies at the heart of peak shift methods such as Kissinger analysis [12,16]. From Eqs. (12b) and (33), we have

$$k_0'\left(\frac{T_\mathrm{p}^2}{\beta}\right)^n \exp\left(-\frac{\Delta H}{k_\mathrm{B}T_\mathrm{p}}\right) = 1. \tag{34}$$

Eq. (34) shows that the temperature, however, at which the maximum in the transformation rate occurs *is* a function of the heating rate: T_p increases as a function of φ. Hence, by measuring T_p for different heating rates, we can obtain ΔH and k_0' from Eq. (34). To do so, we take the logarithm at both sides of Eq. (34) and write

$$\ln\left(\frac{\beta}{T_\mathrm{p}^2}\right) = \frac{1}{n}\ln k_0' - \frac{\Delta H}{nk_\mathrm{B}T_\mathrm{p}}. \tag{35}$$

Having measured $T_\mathrm{p}(\beta)$, we can plot $\ln(\beta/T_\mathrm{p}^2)$ versus $1/T_\mathrm{p}$ (a so-called "Kissinger plot"); this should give a straight line with slope $\Delta H/nk_\mathrm{B}$ that intercepts the vertical axis at $(1/n)\ln k_0'$.

Similarly, it can be shown from Eq. (34) that plots of $\ln(\beta/T_\mathrm{p})$ versus $1/T_\mathrm{p}$ (a Marseglia plot [17]) or simply $\ln(\varphi)$ versus $1/T_\mathrm{p}$ (an Ozawa plot [18,19]) will also give a straight line with the same slope and intersect as Eq. (35), provided Eqs. (6a) and (6b) hold. Thus, all three peak shift methods are formally equivalent in the JMAK framework. This contradicts Baram et al. who claim Ozawa plots are compatible with JMAK kinetics but Kissinger plots are not. The discrepancy is due to the fact that Baram and Erukhimovitch [20] do not use Eqs. (6a) and (6b) throughout their derivation. They implicitly use Eq. (6b) to evaluate the integral in Eq. (3) to correctly show that Ozawa analysis is valid. However, from this it cannot be concluded that Kissinger analysis is *not* valid, as Eqs. (6a) and (6b) imply equivalence of the two methods.

4.2. Determining ΔH, n and k_0'

We can determine ΔH from a measurement of the fraction transformed, $x(t)$, or of the transformation rate, $\mathrm{d}x/\mathrm{d}t$.

Eqs (12a) and (12b) can be rewritten as

$$\ln(-\ln(1-x)) = \ln\left(\frac{k_0'}{\varphi^n}\right) + 2n\ln T - \frac{\Delta H}{k_\mathrm{B}T}. \tag{36}$$

Taking the derivative with respect to $1/T$ gives

$$\frac{\mathrm{d}\ln(-\ln(1-x))}{\mathrm{d}(1/T)} = -2nT - \frac{\Delta H}{k_\mathrm{B}} \approx -\frac{\Delta H}{k_\mathrm{B}}, \tag{37}$$

where again we have used that $\Delta H/2n \gg k_\mathrm{B}T$. Hence, plotting $\ln(-\ln(1-x))$ versus $1/T$ gives a straight line with slope $-\Delta H/k_\mathrm{B}$ that intercepts the vertical axis at $\ln(k_0'/\beta^n)$.

Starting from Eq. (29), it can be shown that

$$\frac{\mathrm{d}\ln(\mathrm{d}x/\mathrm{d}t)}{\mathrm{d}(1/T)} \approx -\frac{\Delta H}{k_\mathrm{B}}(1 - x_\mathrm{e}(t)). \tag{38}$$

Hence, plotting $\ln(\mathrm{d}x/\mathrm{d}t)$ versus $1/T$ gives a curve with a slope equal to $-\Delta H/k_\mathrm{B}$ in the limit $t \to 0$. This result contradicts Henderson's result [12]; he concludes that a plot of $\ln(\mathrm{d}x/\mathrm{d}t)$ versus $1/T$ should give a straight line with a slope approximately equal to $-\Delta H/nk_\mathrm{B}$

(and not $-\Delta H/k_B$). In Appendix B, we explain where we believe that Henderson's derivation goes wrong.

Having obtained values for $\Delta H/n$ and ΔH, we can calculate n.

Knowing n, we obtain k_0' from the intercept with the vertical axis in our Kissinger plot or, alternatively, from the constant in Eq. (36).

It should be noted that it may be more convenient to find the JMAK parameters by fitting Eqs. (12a) and (12b) or (29) to a measurement of $x(t)$ or $dx/dt(t)$, using ΔH, n and k_0' as fit parameters [12].

Obviously, the methods described above only make sense if the transformation follows JMAK kinetics. Methods to check if this is indeed the case are described by Málek [21].

5. The hard impingement approximation

The derivations of the isothermal and linear heating JMAK equations for diffusion-controlled growth are based on the assumption that the growth rate is given by Eq. (25). In the context of nucleation and growth kinetics, this approximation is called the "hard impingement approximation". It ignores the fact that growth will slow down before the particles physically touch, due to the untransformed regions saturating with the element(s) that diffuses away from the interface. Hence, the approximation can only be expected to hold for small x. However, we have seen that, under linear heating conditions, the peak in the transformation rate occurs at $x = 0.63$, which is not small. Hence, Kissinger analysis will only give an approximate value for the $\Delta H/n$ that determines the initial stages of the transformation. Similarly, Eq. (36) will give a curve, with slope equal to $-\Delta H/k_B$ only for small x. The difference between the slope of Eq. (36) at $x = 0$ and at $x = 0.63$ gives a qualitative idea of the inaccuracy of Kissinger analysis. For a more quantitative treatment, Eqs. (1a) and (3) should be solved for diffusion-controlled growth with soft impingement.

6. Conclusions

1. The linear heating JMAK equation can be derived analytically for the same cases and under the same conditions as the isothermal JMAK equation.
2. The JMAK reaction rate equations under isothermal and linear heating conditions are proportional.
3. Isothermal and linear heating transformations are governed by the same effective activation energy, ΔH. The linear heating Avrami exponent is equal to $2n$, where n is the isothermal Avrami exponent. The pre-exponential constants, k_0 and k_0', do not transfer.
4. ΔH and n can be obtained from a linear heating experiment.
5. Peak shift methods such as Kissinger analysis, Marseglia and Ozawa plots are formally equivalent within the JMAK framework and may be used to analyse experimental data.

In this article, we hope to have helped to elucidated a few remaining problems regarding the transferability of the isothermal and linear heating JMAK parameters.

Appendix A

Writing the power series in Eq. (21) as a binomial expansion, we have

$$x_e(t) = \frac{C_0}{\alpha^{bc}} \sum_{j=0}^{\infty} (-1)^j \binom{bc}{j} f^{bc-k}(t) J(t), \tag{A.1}$$

where we have changed the order of integration and summation and defined

$$J(t) \equiv \int_0^t f^j(\tau) \exp\left(-\frac{\varepsilon}{\alpha\tau}\right) d\tau. \tag{A.2}$$

With Eq. (20), we can write Eq. (A.2) as

$$\begin{aligned} J(t) &= \lim_{t'\to 0} \int_{t'}^{t} (\alpha\tau)^{2k} \exp\left(-\frac{j+\varepsilon}{\alpha\tau}\right) d\tau \\ &= -\lim_{t'\to 0} \frac{1}{\alpha^2} \int_{1/t'}^{1/t} \left(\frac{\alpha}{\theta}\right)^{2+2k} \exp\left(-\frac{j+\varepsilon}{\alpha}\theta\right) d\theta \\ &\approx -\lim_{t'\to 0} \frac{1}{\alpha^2} \left(\frac{\alpha}{\theta}\right)^{2+2k} \int_{1/t'}^{1/t} \exp\left(-\frac{j+\varepsilon}{\alpha}\theta\right) d\theta \\ &= \frac{(\alpha t)^{2+2j}}{\alpha(j+\varepsilon)} \exp\left(-\frac{j+\varepsilon}{\alpha t}\right). \end{aligned} \tag{A.3}$$

Putting Eq. (A.3) back into Eq. (A.1) gives

$$\begin{aligned} x_e(t) &= \frac{C_0}{\alpha^{bc}} \sum_{j=0}^{\infty} \binom{bc}{j} \frac{(-1)^k}{\alpha(j+\varepsilon)} (\alpha t)^{2(1+bc)} \\ &\quad \times \exp\left(-\frac{\varepsilon+bc}{\alpha t}\right), \end{aligned} \tag{A.4}$$

where we have substituted Eq. (20). Using Eq. (13) and our abbreviations for C_0, α and ε, and defining

$$C_1(bc,\varepsilon) \equiv \sum_{j=0}^{\infty} \binom{bc}{j} \frac{(-1)^j}{j+\varepsilon}, \tag{A.5}$$

we finally obtain

$$x_e(t) = k_0' \beta^{1+bc} t^{2(1+bc)} \exp\left(-\frac{E_n + bcE_g}{k_B \beta t}\right). \tag{A.6}$$

Appendix B

Henderson starts his derivation from the isothermal JMAK transformation rate equation

$$\frac{dx}{dt}(x) = nk^{1/n}F(x), \tag{B.1}$$

$$k(T) = k_0 \exp\left(-\frac{\Delta H}{k_B T}\right), \tag{B.2}$$

$$F(x) \equiv (1-x)(-\ln(1-x))^{(n-1)/n}. \tag{B.3}$$

Taking the derivative with respect to 1/*T*, gives

$$\frac{d\ln(dx/dt)}{d(1/T)} = -\frac{\Delta H}{nk_B} + \frac{d\ln F(x)}{d(1/T)}. \tag{B.4}$$

He then essentially assumes that the second term on the right hand side in Eq. (B.4) is small compared to the first. However, evaluating the term in question explicitly, gives

$$\frac{d\ln F(x)}{d(1/T)} = \frac{\Delta H}{nk_B} - \frac{\Delta H}{k_B} + \frac{\Delta H}{k_B}\left(\frac{nk_B\beta}{\Delta H}\right)^n kt^{2n}, \tag{B.5}$$

which is by no means small compared to the first term on the right hand side of Eq. (B.4).

Putting Eq. (B.5) back into Eq. (B.4) gives

$$\frac{d\ln(dx/dt)}{d(1/T)} = -\frac{\Delta H}{k_B}\left[1 - \left(\frac{nk_B\beta}{\Delta H}\right)^n kt^{2n}\right]. \tag{B.6}$$

From Eqs. (9) and (13), it can be seen that Eq. (B.6) reduces to Eq. (38) for $E_n = E_g = \Delta H/n$, as it should.

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