ON THE APPLICATION OF THE AVRAMI–EROFEEV EQUATION IN NON-ISOTHERMAL REACTION KINETICS

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ABSTRACT

Generalization of the Avrami–Erofeev equation to non-isothermal solid-state reaction kinetics has been discussed. The derivation of an alternative form of this equation to be used in non-isothermal analyses has been given.

INTRODUCTION

The Avrami–Erofeev equation and related equations [1–3], describing isothermal reaction kinetics in the solid state have often been used in non-isothermal kinetic analyses without further modification [3]. The validity of this procedure has been questioned [4]. Extension of the Avrami–Erofeev equation to non-isothermal conditions has previously been given for special types of solid transformation [3].

In the present article this problem is reformulated, and an alternative form of the extended Avrami–Erofeev equation is derived.

THEORY AND DISCUSSION

Consider a non-isothermal, irreversible reaction based on formation and growth of nuclei in the solid state. The process starts at zero time, and the rate of nucleation, $\dot{N}(y)$, at time y (≥ 0) is assumed to be given by a power law of nucleation, $\dot{N} = k_0(y)y^\sigma$, where $\sigma + 1$ denotes the number of steps in the nucleation [2]. Assuming spherical nuclear growth and ignoring, for the time being, that the growing spheres may overlap, we obtain for the rate of change of reaction volume at time t (and temperature T), $\dot{V} \equiv dV/dt$

$$\dot{V} = \int_0^t \dot{N}(y)k(y)\,dy\,4\pi\left[\int_y^t k(x)\,dx\right]^2$$

$$= 4\pi\int_0^t k_0(y)y^\sigma k(y)\,dy\left[\int_y^t k(x)\,dx\right]^2 \tag{1}$$

The line integral $\int_y^t k(x)\,dx$ is the radius, r, at time t of a sphere nucleated at y. The differential dr is due to a variation dy at y and is defined by

$$dr \equiv \int_y^t k(x)\,dx - \int_{y+dy}^t k(x)\,dx = \int_y^{y+dy} k(x)\,dx = k(y)\,dy$$

This is an inexact differential, contained in eqn. (1). The use of inexact differentials and line integrals in rate expressions, such as eqn. (1), is in agreement with current kinetic theories.

Equation (1) is easily solved at constant temperature (and pressure). To simplify the solution in the non-isothermal case, it is changed into the form

$$\dot V = 4\pi k^3 k_0 \int_0^t y^\sigma \, dy \left\{ \int_y^t \frac{k(x)}{k} \left[\frac{k_0(y)}{k_0} \frac{k(y)}{k} \right]^{1/2} dx \right\}^2 \tag{2}$$

The rate constants k and k_0 are taken to be of the Arrhenius form $k = A \exp(-E/RT)$, etc., so that, by a Taylor series expansion

$$\frac{k(x)}{k} \left[\frac{k(y)}{k} \frac{k_0(y)}{k_0} \right]^{1/2} = \exp\left[-\frac{E}{RT} \frac{T - T(x)}{T(x)} - \frac{E + E_0}{2RT} \frac{T - T(y)}{T(y)} \right]$$

$$= \sum_{i=0}^\infty \frac{1}{i!} \left[-\frac{E}{RT} \frac{T - T(x)}{T(x)} - \frac{E + E_0}{2RT} \frac{T - T(y)}{T(y)} \right]^i \tag{3}$$

Usually, $T - T(x) \ll T(x)$ and $T - T(y) \ll T(y)$, so that the series should converge quite rapidly when E/RT and $(E + E_0)/2RT$ are not too far from unity. Furthermore

$$\frac{1}{T(x)} \equiv \frac{1}{T} \frac{1}{1 - [T - T(x)]/T} = \frac{1}{T} \sum_{n=0}^\infty \left[\frac{T - T(x)}{T} \right]^n \tag{4}$$

a binomial series which normally converges rapidly. However, introducing this expression into the preceding series leads to an unduly complex integral. We therefore use the average of $1/T(x)$ in eqn. (3). This is normally a very good approximation. The average is defined as

$$\left\langle \frac{1}{T(x)} \right\rangle \equiv \frac{1}{t - y} \int_y^t \frac{dx}{T(x)} = \frac{1}{T} \sum_{n=0}^\infty \frac{1}{n+1} \left(\frac{T - T(y)}{T} \right)^n$$

by eqn. (4). $\theta \equiv dT(x)/dx$ is taken to be constant, so that $T - T(y) = \theta(t - y)$. Thus

$$\int_y^t \frac{k(x)}{k}\,dx \left[\frac{k(y)}{k} \frac{k_0(y)}{k_0} \right]^{1/2} = \frac{T}{\theta a} \sum_{i=0}^\infty \frac{1}{(i+1)!} \left(\frac{t - y}{T} \theta \right)^{i+1}$$

$$\times \left[b^{i+1} - (a + b)^{i+1} \right] \tag{5}$$

where $a \equiv -\dfrac{E}{R} \left\langle \dfrac{1}{T(x)} \right\rangle$ and $b \equiv -\dfrac{E + E_0}{2R} \dfrac{1}{T(y)}$. Squaring eqn. (5), re-

arranging and substituting it into eqn. (2) yields, finally

$$\dot{V} = 4\pi k^3 k_0 \int_0^t y^\sigma \frac{dy}{a^2} \sum_{i,j=1}^\infty \left(\frac{t-y}{T}\theta\right)^{i+j} \left[b^i - (a+b)^i\right]\left[b^j - (a+b)^j\right]$$

$$= 4\pi k^3 k_0 \frac{\sigma!}{a^2} t^{\sigma+3} \sum_{i,j=1}^\infty \left(\frac{t\theta}{T}\right)^{i+j-2} \frac{(i+j)!}{i!j!} \frac{\left[b^i - (a+b)^i\right]\left[b^j - (a+b)^j\right]}{(\sigma+i+j+1)!}$$

$$(6)$$

where we have used the integral

$$\int_0^t y^\sigma (t-y)^n \, dy = \frac{n!\sigma!}{(\sigma+n+1)!} t^{\sigma+n+1} \tag{7}$$

a and b have been redefined as

$$a \equiv -\frac{E}{R}\left\langle\left\langle \frac{1}{T(x)}\right\rangle\right\rangle \quad \text{and} \quad b \equiv -\frac{E+E_0}{2R}\left\langle \frac{1}{T(y)}\right\rangle$$

where

$$\left\langle\left\langle \frac{1}{T(x)}\right\rangle\right\rangle \equiv \frac{1}{t}\int_0^t dy \left\langle \frac{1}{T(x)}\right\rangle = \frac{1}{T}\sum_{n=0}^\infty \left(\frac{1}{n+1}\right)^2 \left(\frac{T-T_0}{T}\right)^n$$

by eqn. (4), and

$$\left\langle \frac{1}{T(y)}\right\rangle \equiv \frac{1}{t}\int_0^t \frac{dy}{T(y)} = \frac{1}{T}\sum_{n=0}^\infty \frac{1}{n+1}\left(\frac{T-T_0}{T}\right)^n$$

in analogy with eqn. (4). These are usually very good approximations in eqn. (6).

It is assumed, given the adopted model, that the system would in principle undergo the same physical and chemical (geometric) changes under isothermal conditions. Hence, starting the isothermal reaction at a proper time y_0, we may require the isothermal reaction rate at time t to be equal to that of the actual, non-isothermal process starting at $t = 0$; thus, we require

$$\dot{V}(\text{isothermal}) \equiv \dot{V}(\text{non-isothermal}) \text{ at } t \tag{8}$$

With y_0 as the starting point, we obtain from eqn. (1) at constant temperature, using eqn. (7)

$$\dot{V}(\text{isothermal}) = 4\pi \int_{y_0}^t k_0 k^3 (y-y_0)^\sigma \, dy (t-y_0)^2 = \frac{4\pi\sigma!2!}{(\sigma+3)!} k^3 k_0 (t-y_0)^{\sigma+3}$$

$$(9)$$

Hence, from eqns. (6), (8) and (9)

$$y_0 \equiv t\left\{1 - \left[\frac{(\sigma+3)!}{2!a^2} \sum_{i,j=1}^\infty \frac{(i+j)!}{i!j!}\left(\frac{t\theta}{T}\right)^{i+j-2}\right.\right.$$

$$\left.\left. \times \frac{\left(b^i - (a+b)^i\right)\left(b^j - (a+b)^j\right)}{(\sigma+i+j+1)!}\right]^{1/(\sigma+3)}\right\} \tag{10}$$

Thus, y_0 is a single-valued function of t and T, and $y_0 \geq 0$, when $\theta > 0$. For similar reasons we may also put V(isothermal) $\equiv V$(non-isothermal) at t. Integrating from y_0 to t at constant temperature, we obtain from eqn. (9)

$$V = \frac{4\pi\sigma!2!}{(\sigma+4)!} k^3 k_0 (t - y_0)^{\sigma+4}$$

Obviously, this procedure is simpler than integrating eqn. (6) along a non-isothermal path at constant θ.

If overlap between the growing spheres is to be taken into account, the right-hand side of eqn. (9) has to be multiplied by $V_\infty - V$, [1,2], where V_∞ is the volume when the reaction is completed. Integrating at constant temperature then gives, alternatively

$$-\ln\frac{V_\infty - V}{V_\infty} = \frac{4\pi\sigma!2!}{(\sigma+4)!} k^3 k_0 (t - y_0)^{\sigma+4} \tag{11}$$

where V/V_∞ is the fraction of reaction, α. Equation (11) is an extended version of the Avrami–Erofeev equation to be used in non-isothermal analyses. Inspection shows that the application of these equations requires the overall energy barrier $(3E + E_0)$ to be calculated from non-isothermal data by iteration, assuming starting values of E and E_0 in the expression for y_0.

Equation (10) is well suited for computer calculations. The series converges fairly fast, provided the energy barriers and $\theta t/T$ are not too high. Moreover, the method should be quite accurate, taking the adopted model for granted.

The results obtained depend on the assumed form of the rate constants and nucleation law in addition to spherical growth of the nuclei. A change in these conditions would invalidate the results. It is believed, however, that a similar approach could be adopted in related situations [2], giving rise to similar equations for the non-isothermal case. The isothermal form of the Avrami–Erofeev equation is formally independent of the temperature dependence of the rate constants, but otherwise dependent on nucleation law and the way the nuclei grow.

Considering eqn. (10), we note that θ would have to change with t if T is to be held constant, because of the assumption that $\theta t = T - T_0$ in a single, non-isothermal process. Thus, each point in an isothermal process corresponds in a way to a non-isothermal experiment performed on an identical system at a constant heating rate, different for each point in the isothermal reaction. Thus, the same values of $\dot{V}$ and V, at t, are obtained along these two different paths having the same origin. This is in agreement with the circumstance that $\dot{V}$ and V are state functions (whereas the differential $dV \equiv \dot{V} \, dt$ from eqn. (6) is inexact).

y_0 and related functions have been plotted against time in Fig. 1 for a given set of parameter values. With normal pre-exponential factors, the
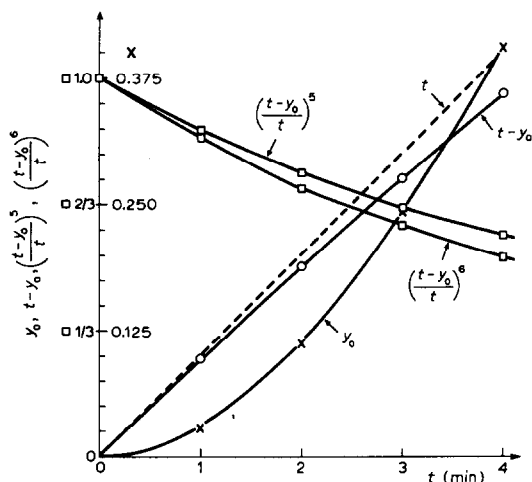
Fig. 1. y_0 and related functions plotted against time. Basic parameter values are as follows: $\sigma = 2$, $\theta = 5$ K min^{-1} and $E/\langle\langle 1/T(x)\rangle\rangle/R = (E + E_0)\langle 1/T(y)\rangle/2R = 10$. $1/T$ in eqn. (10) is put equal to a constant for simplicity: $1/T = 1/500$ K. Terms beyond the fifth in the series in eqn. (10) are ignored: $y_0 \approx t[1 - (1 - 0.15t + 0.130952 \times 10^{-1}t^2 - 0.5357 \times 10^{-3}t^3 + 0.4467 \times 10^{-4}t^4)^{1/5}]$.

reaction should be practically fulfilled within the indicated time span. As might be expected, corrections due to deviations from isothermal conditions become increasingly more important during the reaction. y_0 is an approximate parabola of the form $y = ax^2$.

LIST OF SYMBOLS

t	actual time
x	time ranging from y to t
y	time ranging from 0 to t
T	temperature at t
$T(x), T(y)$	temperature at x, y, respectively
k_0	rate constant of nucleation at t
k	rate constant of nuclear growth at t
r	radius of growing sphere at t
E_0, E	activation energies
A_0, A	pre-exponential factors
θ	heating rate
V	reaction volume at t
$\dot{V}$	rate of volume change at t
$\dot{N}(y)$	rate of nuclear formation at y
σ	constant in power law of nucleation

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