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# SOME COMMENTS ON THE USE OF AVRAMI–EROFEEV EXPRESSIONS AND SOLID STATE DECOMPOSITION RATE CONSTANTS

N. FATEMI *, R. WHITEHEAD, D. PRICE and D. DOLLIMORE **

*Department of Chemistry and Applied Chemistry, University of Salford,
Salford M5 4WT (Gt. Britain)*

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## ABSTRACT

Confusion often arises in the use of Avrami–Erofeev expressions from the lack of common agreement as to the proper definition of the rate constant, made worse by the lack of an agreed definition of a specific rate constant in solid state decomposition studies. The first point is clarified and a specific functional rate constant $k_s$, equal to the fractional decomposition rate at $\alpha = 0.5$, is proposed. Appropriately modified forms of $f(\alpha)$ and $g(\alpha)$, which are consistent with this definition are presented.

## INTRODUCTION

On surveying the literature one can observe the wide use of isothermal and non-isothermal techniques which have been applied extensively to obtain the so called Arrhenius parameters (i.e., activation energy and pre-exponential *A*-factor) for various thermal decomposition reactions of solids. Results obtained by the various methods have produced a spread of values of the Arrhenius or kinetic parameters which cannot be justified on the basis of physico-chemical properties of the solids concerned or, indeed, as an artefact of the instrumental techniques used [e.g., 1–8].

The extensive use over the last two decades of non-isothermal techniques in the study of solid state kinetics has led to the introduction of numerous mathematical methods aimed at obtaining the kinetic parameters from the experimental kinetic data. Widely varying values for the activation energy, *E*, and the pre-exponential factor, *A*, are obtained [9], even from a given set of experimental data especially by those methods which place primary

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Current addresses:
* Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada.
** Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606, U.S.A.

emphasis on the functional form, $f(\alpha)$, supposedly describing the kinetics. More consistent results are obtained by utilizing methods which lay the emphasis on determining $E$ without assigning a particular form to $f(\alpha)$; this has previously been commented upon by a number of workers including the present authors [10,11].

However, in the case of the so-called Avrami–Erofeev expressions [12–14] which have been used extensively, the above confusion has been made worse by a lack of common agreement on the proper definition of the rate constant in the application of these expressions, which are often given as:

$$1-\alpha=e^{-Kt^n} \text{ or } -\ln(1-\alpha)=Kt^n \tag{1}$$

or

$$1-\alpha=e^{-(kt)^n} \text{ or } -\ln(1-\alpha)=(kt)^n \tag{2}$$

where $K$ and $k$ are the rate constants defined by the appropriate equation, $\alpha$ is the fraction decomposed at time $t$ and $n$ is a constant which in terms of the Avrami model is given by

$$n=\beta+\lambda$$

where $\beta$ is the number of steps for the production of stable product nuclei and $\lambda$ is the number of dimensions in which the product nuclei grow.

## METHODS

Equations (1) and (2) in their differential forms may be written as:

$$d\alpha/dt=nK^{1/n}(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{3}$$

and

$$d\alpha/dt=nk(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{4}$$

The study of the literature has shown that confusion exists as to which one of the integral and/or differential forms should be used to evaluate the specific rate constants and hence the kinetic parameters via the Arrhenius equation which expresses the rate constant $k_A$ in the form:

$$k_A=A\exp(-E/RT) \tag{5}$$

The solid state decomposition rate constant, $k$, is defined by the expression

$$\frac{d\alpha}{dt}=kf(\alpha) \tag{6}$$

where $k$ has units of reciprocal time. By comparison with eqn. (4) an obvious choice is

$$k_A=k \tag{7}$$

with

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{8}$$

Hence the values of the kinetic parameters obtained utilizing

$$k = A\exp(-E/RT) \tag{9}$$

will be the values consistent with the definition of the rate constant in eqns. (6–8).

If values of the equations for $K$ (1) and (3) have been used to obtain the kinetic parameters, then as

$$K = (k)^n \tag{10}$$

and

$$\begin{aligned}(k)^n &= A^n(\exp(-E/RT))^n\\ &= A^n\exp(-nE/RT)\end{aligned} \tag{11}$$

then the apparent values, $A_K$ and $E_K$, calculated via the Arrhenius equation for the temperature dependence of $K$ are related to the proper empirical (see eqn. 6) values in the manner

$$A_K = A^n \tag{12}$$

and

$$E_K = nE \tag{13}$$

It is interesting to see the difference which would ensue if $f^*(\alpha)$, given by

$$f(\alpha) = nf^*(\alpha) \tag{14}$$

is used in the treatment of the experimental data. In terms of expressions (2) and (4) this amounts to putting

$$k^* = nk = nk_A \tag{15}$$

hence the apparent pre-exponential factor, $A^*$, will be related to the original one as

$$A^* = nA \tag{16}$$

It should be noted however, that the activation energy will remain unchanged, i.e., $E^* = E$. This leads to the question of which value of the pre-exponential factor should be preferred and why, in any case, should such ambiguities arise?

To help resolve these questions it is first useful to consider kinetic rate equations in the gas or solution phase. For example, for a second order rate process

$$B + B \rightarrow \text{Products}$$

the rate equation would normally be written in the form

$$-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_s[\mathrm{B}]^2 \tag{17}$$

where $k_s$ is the specific rate constant, i.e., it is numerically equal to the rate at unit concentration (or unit activity, pressure etc.). The units of $k_s$ are time$^{-1}$ concentration$^{-1}$; differing units for the concentrations would of course lead to different numerical values for $k_s$ and hence the pre-exponential factor; though of course, these different values would be simply and unambiguously related to each other. The second order rate eqn. (17) cannot be rendered into a non-dimensional form in contrast to solid state rate equations which are invariably stated in non-dimensional form in terms of the fractional decomposition, $\alpha$. However the first order rate equation corresponding to a reaction

B → Products

which may be written as

$$-\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_s[\mathrm{B}] \tag{18}$$

can also be written in terms of the fraction, $\alpha$ of B which has reacted, viz.

$$-\frac{\mathrm{d}[\mathrm{B}]_0(1-\alpha)}{\mathrm{d}t} = k_s(1-\alpha)[\mathrm{B}]_0 \tag{19}$$

where $[\mathrm{B}]_0$ is the initial concentration of B, hence

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_s(1-\alpha) \tag{20}$$

and $k_s$ remains the specific rate constant, i.e., the fractional rate at unit concentration. From eqn. (20) it can be seen that $k_s$ also equals the fractional rate of decomposition when $\alpha = 0$. Thus it might be thought useful to make a definition of a specific fractional decomposition rate constant at $\alpha = 0$, zero decomposition. However, the functional forms of $f(\alpha)$ in a number of commonly used cases are not amenable to such a choice as the $f(\alpha) \to 0$ as $\alpha \to 0$; the Avrami–Erofeev expressions are a particular example of this behaviour.

Now it is well known that in the mid-range of decomposition, say $0.4 < \alpha < 0.6$, most solid state decompositions show a reasonable approximation to first order behaviour which suggests that it might be appropriate to use the midpoint of decomposition, $\alpha = 0.5$, to define solid state decomposition rate constants. This can be simply achieved by the statement: "*The specific fractional decomposition rate constant $k_s$ shall equal the fractional decomposition rate at $\alpha = 0.5$, the mid point of the decomposition; the proper choice of the multiplicative constant in $f(\alpha)$ must be consistent with this property, i.e., $f(0.5) = 1$.*"

## RESULTS AND DISCUSSION

In many cases, especially in the treatment of non-isothermal kinetic data, it is the integrated form of the rate equation which is utilized, i.e.,

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha'}{\mathrm{f}(\alpha')} = \int_0^{t} k(T) \cdot \mathrm{d}t \tag{21}$$

and the function $\mathrm{g}(\alpha)$ is defined as

$$\mathrm{g}(\alpha) \equiv \int_0^{\alpha} \frac{\mathrm{d}\alpha'}{\mathrm{f}(\alpha')} \tag{22}$$

Under isothermal conditions (21) immediately gives

$$\mathrm{g}(\alpha) = kt \tag{23}$$

but under non-isothermal conditions the right hand side of (21) must be evaluated using the appropriate dependence of temperature on time; e.g., for a linear heating rate

$$T = T_0 + \beta t \tag{24}$$

where $\beta$ is the constant heating rate. In Table 1 the usual forms for $\mathrm{f}(\alpha)$ and $\mathrm{g}(\alpha)$ are given for a number of commonly occurring cases.

Table 2 lists the appropriately modified forms of $\mathrm{f}(\alpha)$ and $\mathrm{g}(\alpha)$ which are consistent with the present proposed definition of the specific fractional decomposition rate constant. In terms of the consistency currently achieved with respect to the kinetic parameters, especially the $A$ factors, the proposed

TABLE 1

Commonly used kinetic expressions for solid-state decompositions $A(\alpha)$, $R(\alpha)$, $D(\alpha)$ and $F(\alpha)$ are the labels used by Sharp et al. [17]

| Mechanism | Integral form $\mathrm{g}(\alpha)$ | $\mathrm{f}(\alpha)$ |
|---|---|---|
| Power Law | $\alpha^{1/s} = kt$ | $s\alpha^{(1-1/s)}$ |
| Exponential law | $\ln \alpha - \ln \alpha_0 = k(t - t_0)$ | $\alpha$ |
| Avrami–Erofeev, $A_2(\alpha)$ | $[-\ln(1-\alpha)]^{1/2} = kt$ | $2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ |
| Avrami–Erofeev, $A_3(\alpha)$ | $[-\ln(1-\alpha)]^{1/3} = kt$ | $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ |
| Contracting sphere (Mample), $R_3(\alpha)$ | $1-(1-\alpha)^{1/2} = kt$ | $2(1-\alpha)^{1/2}$ |
| Contracting sphere (Mample), $R_3(\alpha)$ | $1-(1-\alpha)^{1/3} = kt$ | $3(1-\alpha)^{2/3}$ |
| Ginstling–Brounshtein, $D_4(\alpha)$ | $(1-2\alpha/3)-(1-\alpha)^{2/3} = kt$ | $3/2[(1-\alpha)^{-1/3}-1]^{-1}$ |
| One dimensional diffusion, $D_1(\alpha)$ | $\alpha^2 = kt$ | $1/2.\alpha^{-1}$ |
| Two dimensional diffusion, $D_2(\alpha)$ | $(1-\alpha)\ln(1-\alpha)+\alpha = kt$ | $[-\ln(1-\alpha)]^{-1}$ |
| Three dimensional diffusion, $D_3(\alpha)$ | $[1-(1-\alpha)^{1/2}]^2 = kt$ | $3/2(1-\alpha)^{2/3} \times [1-(1-\alpha)^{1/3}]^{-1}$ |
| First order decay, $F_1(\alpha)$ | $-\ln(1-\alpha) = kt$ | $(1-\alpha)$ |
| Second order | $(1-\alpha)^{-1}-1 = kt$ | $(1-\alpha)^2$ |
| Third order | $1/2[(1-\alpha)^{-2}-1] = kt$ | $(1-\alpha)^3$ |

TABLE 2

Functional forms of $f(\alpha)$ and $g(\alpha)$ compatible with proposed definition for the specific fractional decomposition rate constant $k_s$

| Mechanism | $g(\alpha) = d.g^*(\alpha) = k_s t$ | | $f(\alpha) = c.f^*(\alpha)$ | |
|---|---|---|---|---|
| | $d$ | $g^*(\alpha)$ | $c$ | $f^*(\alpha)$ |
| Power law | $s/2^{(1-1/s)}$ | $\alpha^{1/s}$ | $2^{(1-1/s)}$ | $\alpha^{(1-1/s)}$ |
| Exponential law | 0.5000 | $[\ln \alpha - \ln \alpha_0]$ | 2.000 | $\alpha$ |
| Avrami–Erofeev | 0.8326 | $[-\ln(1-\alpha)]^{1/2}$ | 2.402 | $(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ |
| Avrami–Erofeev | 1.175 | $[-\ln(1-\alpha)]^{1/3}$ | 2.554 | $(1-\alpha)[-\ln(1-\alpha)]^{2/3}$ |
| Contracting area | 1.414 | $[1-(1-\alpha)^{1/2}]$ | 1.414 | $(1-\alpha)^{1/2}$ |
| Contracting sphere | 1.890 | $[1-(1-\alpha)^{1/3}]$ | 1.587 | $(1-\alpha)^{2/3}$ |
| Ginstling–Brounshtein | 5.771 | $[(1-2\alpha/3)-(1-\alpha)^{2/3}]$ | 0.2599 | $[1-(1-\alpha)^{-1/3}-1]^{-1}$ |
| One dimensional diffusion | 1.000 | $\alpha^2$ | 0.5000 | $1/\alpha$ |
| Two dimensional diffusion | 1.443 | $[(1-\alpha)\ln(1-\alpha)+\alpha]$ | 0.6931 | $[-\ln(1-\alpha)]^{-1}$ |
| Three dimensional diffusion | 4.580 | $[1-(1-\alpha)^{1/3}]^2$ | 0.3275 | $(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$ |
| First order decay | 0.5000 | $[-\ln(1-\alpha)]$ | 2.000 | $(1-\alpha)$ |
| Second order | 0.2500 | $[(1-\alpha)^{-1}-1]$ | 4.000 | $(1-\alpha)^2$ |
| Third order | 0.0625 | $[(1-\alpha)^{-2}-1]$ | 8.000 | $(1-\alpha)^3$ |

definition of the specific rate constant will not usually make a significant numerical difference. However, it is nevertheless desirable that all data should be treated on a common and unambiguous basis.

It is appropriate at this juncture to comment on the practical use of Avrami–Erofeev expressions in terms of the experimental kinetic data. Frequently this involves again taking logarithms of (2) to give:

$$\ln[-\ln(1-\alpha)] = n \ln k + n \ln t \tag{25}$$

Not surprisingly it is generally found that plots of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ produce straight lines in the range $0.15 < \alpha < 0.85$, e.g. [14–16]. However, it must be pointed out that for the optimal determination of the rate constant it is best to avoid direct use of expression (25), the result of double logarithmization. Such plots should be used to find the experimental value of $n$ from the slope; once the value of $n$ is determined a plot of $\ln(\frac{1}{1-\alpha})$ versus $t^n$ allows $k^n$, and hence $k$, to be found from the slope, rather than from the intercept.

## CONCLUSION

To conclude it is worth considering how kinetic parameters obtained on the basis of the Avrami–Erofeev expressions relate to the kinetic parameters of the Avrami model [12]. It is said that the usual Avrami–Erofeev expressions are of considerable interest to solid-state chemists because they allow the $\alpha$ versus $t$ plots to be understood in Avrami model terms. Thus it is of importance carefully to consider conditions under which the Avrami model gives rise to expressions of the Avrami–Erofeev type and on the other hand when the application of such expressions is, in principle, entirely empirical. The present authors have considered this question in some detail and hope to publish the results in a forthcoming paper.

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