Combined Kinetic Analysis of Solid-State Reactions: A Powerful Tool for the Simultaneous Determination of Kinetic Parameters and the Kinetic Model without Previous Assumptions on the Reaction Mechanism

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TABLE 1: Algebraic Expressions for the $f(\alpha)$ Functions for the Most Common Mechanisms in Solid-State Reactions and Their Corresponding Equivalent Reduced Sestak−Berggren Equations

mechanism	symbol	$f(\alpha)$	equivalent reduced Sestak−Berggren equation
phase boundary controlled reaction (contracting area, i.e., bidimensional shape)	R2	$(1-\alpha)^{1/2}$	$(1-\alpha)^{1/2}$
phase boundary controlled reaction (contracting volume, i.e., tridimensional shape)	R3	$(1-\alpha)^{2/3}$	$(1-\alpha)^{2/3}$
unimolecular decay law (instantaneous nucleation and unidimensional growth)	F1	$(1-\alpha)$	$(1-\alpha)$
random instant nucleation and two-dimensional growth of nuclei (Avrami−Erofeev equation)	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2.079(1-\alpha)^{0.806}\alpha^{0.515}$
random instant nucleation and three-dimensional growth of nuclei (Avrami−Erofeev equation)	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3.192(1-\alpha)^{0.748}\alpha^{0.693}$
two-dimensional diffusion (bidimensional particle shape)	D2	$1/[-\ln(1-\alpha)]$	$0.973(1-\alpha)^{0.425}\alpha^{-1.008}$
three-dimensional diffusion (tridimensional particle shape) Jander equation	D3	$[3(1-\alpha)^{2/3}]/\{2[1-(1-\alpha)^{1/3}]\}$	$4.431(1-\alpha)^{0.951}\alpha^{-1.004}$

Reproduce figure 1 of the paper to show that the algebraic expressions are indeed equated by the equivalent reduced Sestak-Berggren equations listed in Table 1

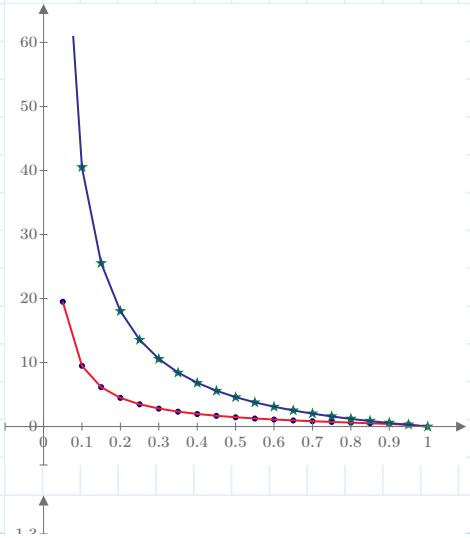
$$f\_D2(\alpha) := \frac{1}{-\ln(1-\alpha)} \qquad f\_SBD2(\alpha) := 0.973\ (1-\alpha)^{0.425}\cdot\alpha^{-1.008}$$

$$f\_D3(\alpha) := \frac{3\cdot(1-\alpha)^{\frac{2}{3}}}{2\cdot\left(1-(1-\alpha)^{\frac{1}{3}}\right)} \qquad f\_SBD3(\alpha) := 4.431\ (1-\alpha)^{0.951}\cdot\alpha^{-1.004}$$

$$f\_A2(\alpha) := 2\ (1-\alpha)\cdot(-\ln(1-\alpha))^{\frac{1}{2}} \qquad f\_SBA2(\alpha) := 2.079\ (1-\alpha)^{0.806}\cdot\alpha^{0.515}$$

$$f\_A3(\alpha) := 3\ (1-\alpha)\cdot(-\ln(1-\alpha))^{\frac{2}{3}} \qquad f\_SBA3(\alpha) := 3.192\ (1-\alpha)^{0.748}\cdot\alpha^{0.693}$$

$$\alpha := 0, 0.05 .. 1.00$$

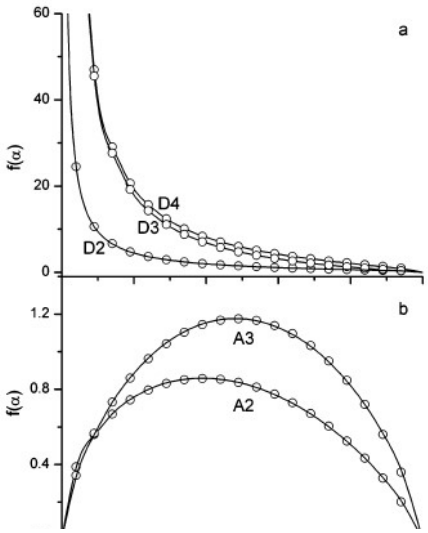


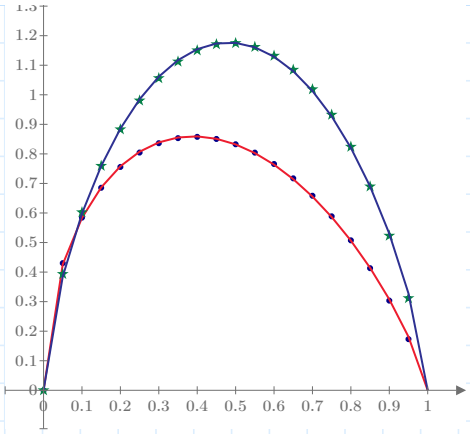
$f\_D2(\alpha)$

$f\_SBD2(\alpha)$

$f\_D3(\alpha)$

$f\_SBD3(\alpha)$





$f\_A2(\alpha)$

$f\_SBA2(\alpha)$

$f\_A3(\alpha)$

$f\_SBA3(\alpha)$

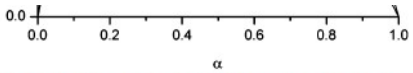


Figure 1. Comparison of the $f(\alpha)$ (dots) corresponding to diffusion (a) and nucleation–growth (b) mechanisms with the Sestak–Berggren equations with the corresponding n and m parameters tabulated in Table 1 (solid lines).

Paper uses a reduced Sestak-Berggren equation $f(\alpha) = c \cdot (1-\alpha)^n \cdot \alpha^m$ with the three parameters c,n,m to equate to the model algebraic equation. The problem of determining the three parameters is listed in the paper as a multiphase process involving the use of an optimising process that maximizes the Pearson's linear correlation coefficient.

In this worksheet it is shown that a simpler general curve fitting function using "genfit()" from PTC Prime produces a near perfect fit for the model algebraic equation with a Pearson's linear correlation coefficient of close to perfect at 1.000 the maximum.

$\mathbf{ORIGIN} := 1$

Set up the x values:

$i := 1 \,..\, 19$ $\qquad$ $\alpha_i := 0.05 \cdot i$

Set up the y values and define the fitting function:

$\phi_i := f\_D3(i \cdot 0.05)$ $\qquad$ $\varphi(\alpha i, c, n, m) := c \cdot (1-\alpha i)^n \cdot (\alpha i)^m$

Find the partial derivatives of the fitting function for genfit() function argument:

$$\frac{\partial}{\partial c}\varphi(ai, c, n, m) \rightarrow (-ai+1)^n \cdot ai^m$$

$$\frac{\partial}{\partial n}\varphi(ai, c, n, m) \rightarrow c \cdot \ln(-ai+1) \cdot (-ai+1)^n \cdot ai^m$$

$$\frac{\partial}{\partial m}\varphi(ai, c, n, m) \rightarrow c \cdot \ln(ai) \cdot (-ai+1)^n \cdot ai^m$$

$$F(ai, cnm) := \begin{bmatrix} cnm_1 \cdot (1-ai)^{cnm_2} \cdot (ai)^{cnm_3} \\ (-ai+1)^{cnm_2} \cdot ai^{cnm_3} \\ cnm_1 \cdot \ln(-ai+1) \cdot (-ai+1)^{cnm_2} \cdot ai^{cnm_3} \\ cnm_1 \cdot \ln(ai) \cdot (-ai+1)^{cnm_2} \cdot ai^{cnm_3} \end{bmatrix}$$

Apply the genfit() function and see is close to Table 1 values:

$$\begin{bmatrix} c \\ n \\ m \end{bmatrix} := \text{genfit}\left(\alpha, \phi, \begin{bmatrix} 1.0 \\ 1.0 \\ 1.0 \end{bmatrix}, F\right) = \begin{bmatrix} 4.4182 \\ 0.9475 \\ -1.0053 \end{bmatrix} \qquad 4.431(1-\alpha)^{0.951}\alpha^{-1.004}$$

Test the correlation coefficient of the reduced equation:

$$vy_i := F\left(\alpha_i, \begin{bmatrix} 4.4182 \\ 0.9475 \\ -1.0053 \end{bmatrix}\right)_1$$

$$\mathrm{corr}(\phi, vy) = 0.99999916$$

Test the correlation coefficient of the Table 1 values:

$$vy_i := F\left(\alpha_i, \begin{bmatrix} 4.431 \\ 0.951 \\ -1.004 \end{bmatrix}\right)_1 \qquad \mathrm{corr}(\phi, vy) = 0.99999898$$

Set up another set of y values and fit the reduced equation to the data:

$$\phi_i := f\_A3(i \cdot 0.05)$$

$$\begin{bmatrix} c \\ n \\ m \end{bmatrix} := \mathrm{genfit}\left(\alpha, \phi, \begin{bmatrix} 0.5 \\ 0.5 \\ 0.5 \end{bmatrix}, F\right) = \begin{bmatrix} 3.2007 \\ 0.7501 \\ 0.6948 \end{bmatrix} \qquad 3.192(1-\alpha)^{0.748}\alpha^{0.693}$$

$$vy_i := F\left(\alpha_i, \begin{bmatrix} 3.2007 \\ 0.7501 \\ 0.6948 \end{bmatrix}\right)_1$$

$$\mathrm{corr}(\phi, vy) = 0.99978607$$