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Note

DETERMINATION OF THE KINETICS AND MECHANISM OF A SOLID STATE REACTION. A SIMPLE APPROACH

A.B. PHADNIS and V.V. DESHPANDE

Reactor Chemistry Section, Chemical Group, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

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Many mathematical methods have been postulated in the literature [1] for the determination of the kinetics and mechanism of a solid state reaction from thermoanalytical curves obtained either isothermally or non-isothermally.

These methods are based on the use of the basic rate equation

$$\frac{d\alpha}{dt} = K f(\alpha) = Z\,e^{-E/RT} f(\alpha) \qquad \text{(Isothermal)} \qquad (1)$$

or, changing the variables from time to temperature

$$\frac{d\alpha}{dT} = \frac{K}{\beta} f(\alpha) = \frac{Z\,e^{-E/RT}}{\beta} f(\alpha) \qquad \text{(Non-isothermal)} \qquad (2)$$

By using any of these equations, either in the differential form, as given, or in the integral form

$$g(\alpha) = Kt = Z\,e^{-E/RT} t \qquad (3)$$

or

$$g(\alpha) = \frac{ZRT^2}{\beta E}\left[1 - \frac{2RT}{E}\right] e^{-E/RT} \qquad (4)$$

for isothermal and non-isothermal procedures, respectively, and plotting the logarithmic version of either of these equations, the kinetic parameters are generally evaluated.

The values of E, Z and K, thus obtained, become the kinetic parameters and the functional form of α, i.e. $f(\alpha)$ or its integral form $g(\alpha)$, become the mechanism determining function for a reaction under investigation. Often the logarithmic version of the differential or integral form of the equation for any functional form $f(\alpha)$ or $g(\alpha)$, when plotted against the reciprocal of temperature, $1/T$, becomes more or less linear and it becomes very difficult to decide the validity of a particular mechanism for a reaction under investigation and also the real kinetic parameters.

In view of this, quite a few procedures have been suggested in the

TABLE 1

Values of f(α), g(α) and g′(α) for different solid state reaction mechanisms

Reaction mechanism	f(α)	g(α)	g′(α)
1. Power law	$1/r\,\alpha^{1-r}$	α^r	$r \ln \alpha$, ($r=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 1, \frac{3}{2}$ or 2)
2 Nucleation and nuclei growth			
Random nucleation (Mampel unimolecular law)	$(1-\alpha)$	$-\ln(1-\alpha)$	$\ln[-\ln(1-\alpha)]$
Avrami–Erofeev nuclei growth	$1/r(1-\alpha)[-\ln(1-\alpha)]^{1-r}$	$[-\ln(1-\alpha)]^r$	$r \ln[-\ln(1-\alpha)]$, ($r=\frac{1}{4}, \frac{1}{3}, \frac{1}{2}$ or $\frac{2}{3}$)
Prout–Tompkins branching nuclei	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	$\ln \ln[\alpha/(1-\alpha)]$
3. Diffusion controlled			
Jander, 3-dimensional diffusion	$(1-\alpha)^{-1/3}[1-(1-\alpha)^{-1/3}]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$	$2\ln[1-(1-\alpha)^{1/3}]$
Anti-Jander, 3-dimensional counter diffusion.	$(1+\alpha)^{1/3}[1-(1+\alpha)^{-1/3}]^{-1}$	$\frac{3}{2}[(1+\alpha)^{1/3}-1]^2$	$2\ln[(1+\alpha)^{1/3}-1]$
Brounshtein–Ginstling, 3-dimensional diffusion	$[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}]$	$\ln[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}]$
Valensi, 2-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	$\ln[(1-\alpha)\ln(1-\alpha)+\alpha]$
4. Exponential	$1/r\,\alpha$	$\ln \alpha^r$	$r \ln \ln \alpha$, ($r=1$ or 2)
5. Phase boundary			
Contracting sphere	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	$\ln[1-(1-\alpha)^{1/3}]$
Contracting cylinder	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	$\ln[1-(1-\alpha)^{1/2}]$
6. Reaction order	$\frac{1}{2}(1-\alpha)^{1-r}$	$1-(1-\alpha)^r$	$\ln[1-(1-\alpha)^r]$($r=2, 3,$ or 4)

literature. Amongst these are (a) generation of theoretical thermoanalytical curves for different functional forms of α and their comparison with experimental curves [2–4], (b) comparison of isothermally and non-isothermally determined functional curves [5,6], and (c) comparison of differential and integral methods, selecting the matching parameters [7,8], and determining the functional form of α, i.e. $f(\alpha)$.

The determination of theoretical thermoanalytical curves for all possible functional forms of α, $f(\alpha)$, and their comparison with experimental curves is a very elaborate exercise. On several occasions, the determination of the isothermal curve is not possible because of the limitations of the experimental set-up and also the time involved. Similarly, determining kinetic parameters by differential as well as integral methods does not mean different results, since these originate from the same basic equations [eqn. (1) or (2)].

It is, however, possible to remodel eqn. (4) by substituting eqn. (2) and rearranging it to give

$$f(\alpha)\, g(\alpha) = \frac{RT^2}{E}\left[1 - \frac{2RT}{E}\right]\frac{d\alpha}{dT} \tag{5}$$

On neglecting the comparatively small term $2R^2T^3/E^2$, eqn. (5) reduces to

$$f(\alpha)\, g(\alpha) = \frac{RT^2}{E}\,\frac{d\alpha}{dT} \tag{6}$$

A linearity of plot of $f(\alpha)$, $g(\alpha)$ vs. $T^2\, d\alpha/dT$ or any other combination

TABLE 2

Values of fraction conversion, α, with respect to reciprocal temperature, $1/T$ for $CdCO_3$ decomposition

α	$1/T \times 10^3$
0	1.538
0.0046	1.508
0.0172	1.484
0.0406	1.458
0.0788	1.431
0.1352	1.401
0.2200	1.381
0.3405	1.359
0.5025	1.337
0.6993	1.314
0.9015	1.292
0.9883	1.285
1.0000	1.274

can decide the mechanism determining the functional form of α.

Alternatively, on integration of eqn. (6), we have

$$g'(\alpha) = -\frac{E}{RT} \tag{7}$$

where $g'(\alpha) = \int f(\alpha)\, g(\alpha)\, d\alpha$.

The plot of $g'(\alpha)$ vs. $1/T$ is linear with the proper functional form of α. The slope of this plot, if multiplied by R, gives the value of E. Application of this new method clearly gives a means of obtaining the valid reaction mechanism.

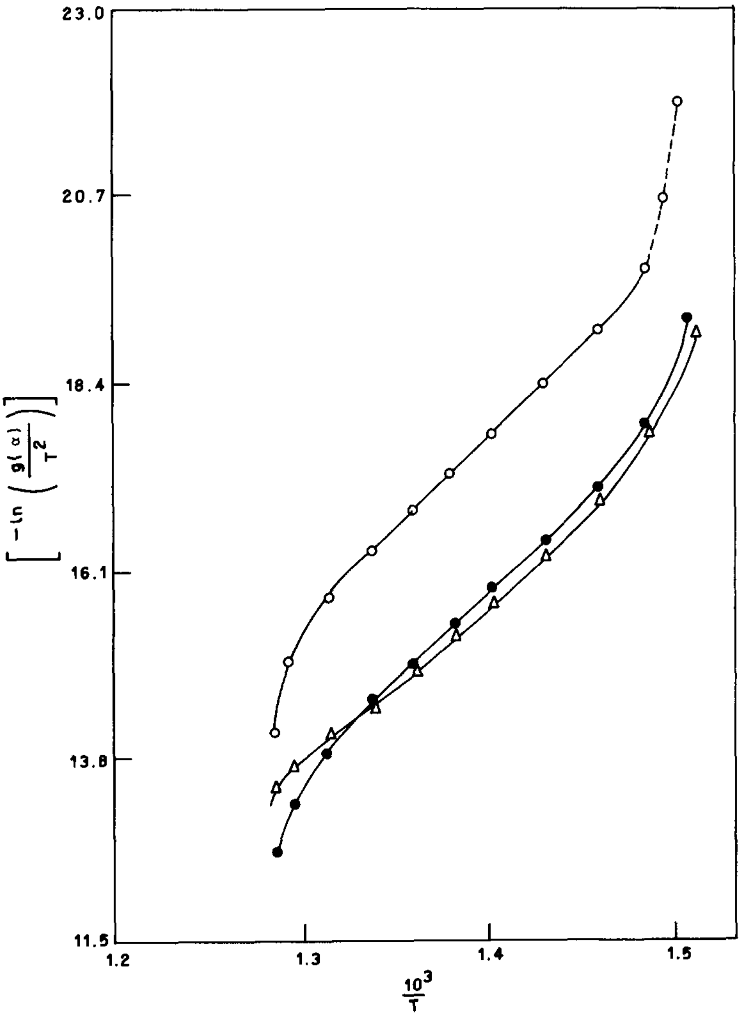

Fig. 1. Coats and Redfern [10] plot for $CdCO_3$ decomposition. ○, $g(\alpha) = [1-(1-\alpha)^{1/3}]$; Δ, $g(\alpha) = [1-(1-\alpha)^{1/2}]$; ●, $g(\alpha) = [1-\ln(1-\alpha)]$.

Different g′(α) values, along with f(α) and g′(α) values, applicable for various reaction mechanisms of a solid state reaction, are given in Table 1 for convenience.

The applicability of this new method is illustrated by studying the thermal decomposition of $CdCO_3$. The different values of fractional conversion, α, with respect to reciprocal of temperature, $1/T$, required for this reaction to show the linearity limits of different plots in ensuing figures, are given in Table 2.

The decomposition of $CdCO_3$ to CdO and CO_2 has an order of 0.5 [9] and has a phase boundary controlled contracting cylinder mechanism reaction. When the logarithmic version of the Coats and Redfern method [10], i.e. $\ln[g(\alpha)/T^2]$, is plotted with respect to $1/T$ for a 0.5 order or phase boundary controlled cylindrical mechanism, a 0.67 order or phase boundary controlled spherical mechanism, a first order or nucleation and growth random nucleation mechanism (Mampel unimolecular law), all plots become

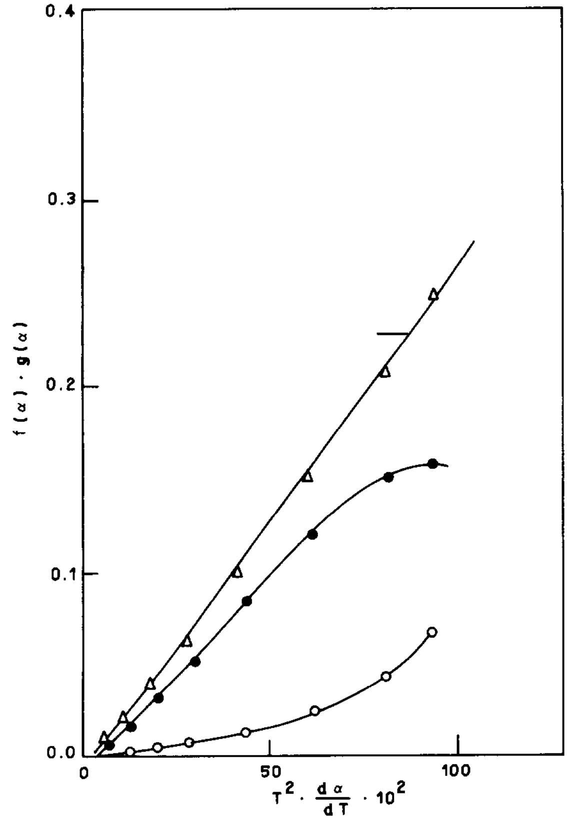

Fig. 2. Plot according to eqn. (6) for $CdCO_3$ decomposition. ○, $f(\alpha) = (1-\alpha)^{2/3}$, $g(\alpha) = 3[1-(1-\alpha)^{1/3}]$; Δ, $f(\alpha) = (1-\alpha)^{1/2}$, $g(\alpha) = 2[1-(1-\alpha)^{1/2}]$; ●, $f(\alpha) = (1-\alpha)$, $g(\alpha) = [-\ln(1-\alpha)]$.

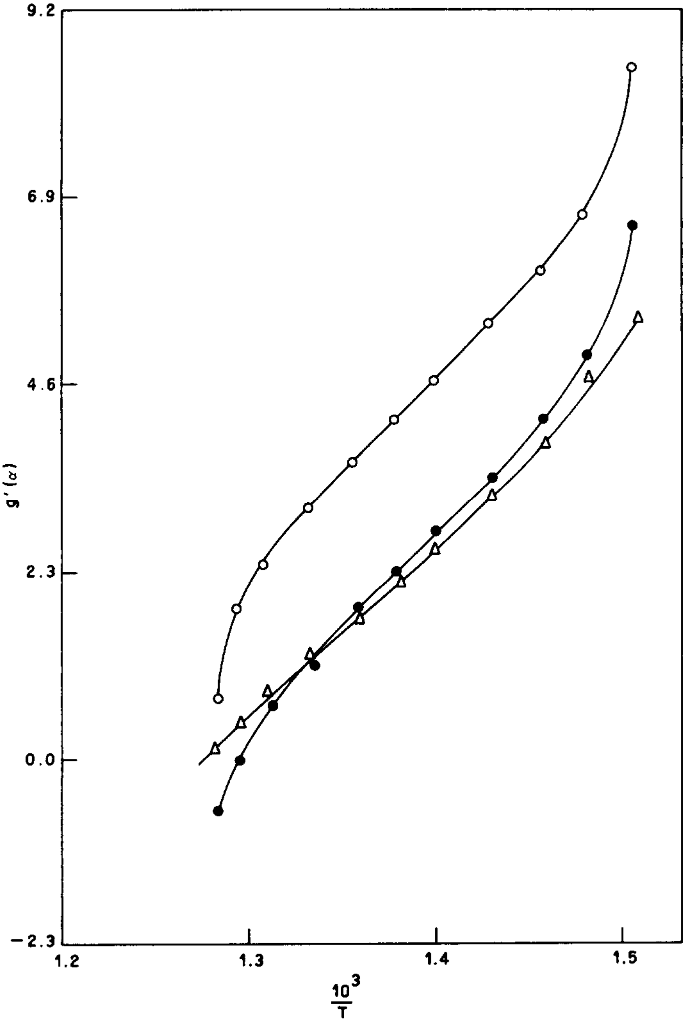

Fig. 3. Plot according to eqn. (7) for $CdCO_3$ decomposition. ○, $g'(\alpha) = -\ln[1-(1-\alpha)^{1/3}]$; Δ, $g'(\alpha) = -\ln[1-(1-\alpha)^{1/2}]$; ●, $g'(\alpha) = -\ln[-\ln(1-\alpha)]$.

linear ($\alpha \simeq 0.05$–0.75). It becomes very difficult to distinguish which particular mechanism is valid (Fig. 1) but when our new method is followed, one can pinpoint the difference between different reaction mechanisms [Fig. 2, eqn. (6) and Fig. 3, eqn. (7)]. Here the plot is linear for 0.5 order or phase boundary controlled cylindrical mechanism only.

It is pointed out that it is a very simple approach to use either eqn. (6) or (7) for the determination of the proper reaction mechanism for all possible functional forms of α, i.e. $f(\alpha)$ $g(\alpha)$ in the case of eqn. (6) and $g'(\alpha)$ in the case of eqn. (7) and check the linearity of the plots for non-isothermally determined solid state reaction.

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