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Note

Evaluation of kinetic parameters from thermogravimetric curves

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Several different methods have been proposed[1, 2] for treating the experimentally recorded thermogravimetric (TG) curves of decomposition reactions to extract the kinetic parameters. Among them the empirical equation of Coats and Redfern[3] has been widely employed. The equation expressed in the most general form can be written as

$$\log\left[\frac{g(\alpha)}{T^2}\right] = -\frac{E}{2.3\,RT} + \log\frac{ZR}{\beta E}\left[1 - \frac{2RT}{E}\right] \tag{1}$$

where β is the linear heating rate, E is the apparent activation energy and Z is the pre-exponential factor of the Arrhenius equation. In all the analyses of the thermogravimetric curves the linearity criterion of $\log\,[g(\alpha)/T^2]$ vs. $1/T$ is taken as sufficient proof for the correct form of $g(\alpha)$ and hence the model of the reaction mechanism proposed. However recently Criado and Morales[4], based on their theoretical analysis, have concluded that this linearity of $\log\,[g(\alpha)/T^2]$ vs. $1/T$ is a necessary but not a sufficient criterion to assign an unequivocal $g(\alpha)$ function. They have shown that $g(\alpha) = [-\log\,(1-\alpha)]^{1/n}$, yielded about the same linear correlation between $\log\,[g(\alpha)/T^2]$ vs. $1/T$ for $n = 1$, 2 or 3. They therefore reiterated the necessity of recording at least one isothermal run of the same reaction in the temperature interval of the TG measurement in order to assign the proper $g(\alpha)$ form. We present in this paper experimental data on the decomposition of $CdCO_3$ which supports their theoretical analysis.

Thermogravimetric curves (Fig. 1) for the decomposition of $CdCO_3$ on small (~ 3 mg) samples were obtained in a flowing stream of argon at a 5° min^{-1} heating rate using the microthermobalance constructed in our laboratory[5].

The TG curves were analysed assuming the Avrami and Erofeyev[6, 7] relation for $g(\alpha)$ as

$$g(\alpha) = [-\log\,(1-\alpha)]^{1/n} \tag{2}$$

for $n = 1, 2$ and 3. These plots of $\log\,[g(\alpha)/T^2]$ vs. $1/T$ are shown in Fig. 2. As can be

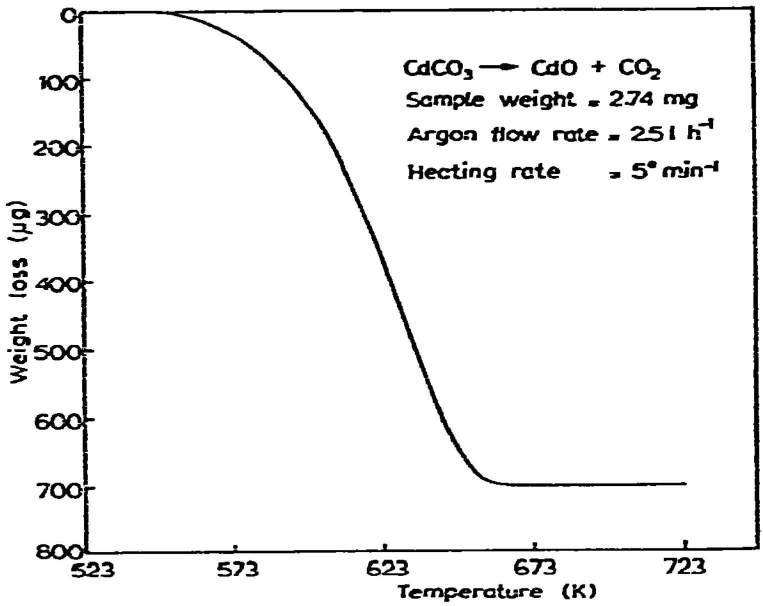

Fig. 1. Thermogravimetric curve for the decomposition of $CdCO_3$ in argon.

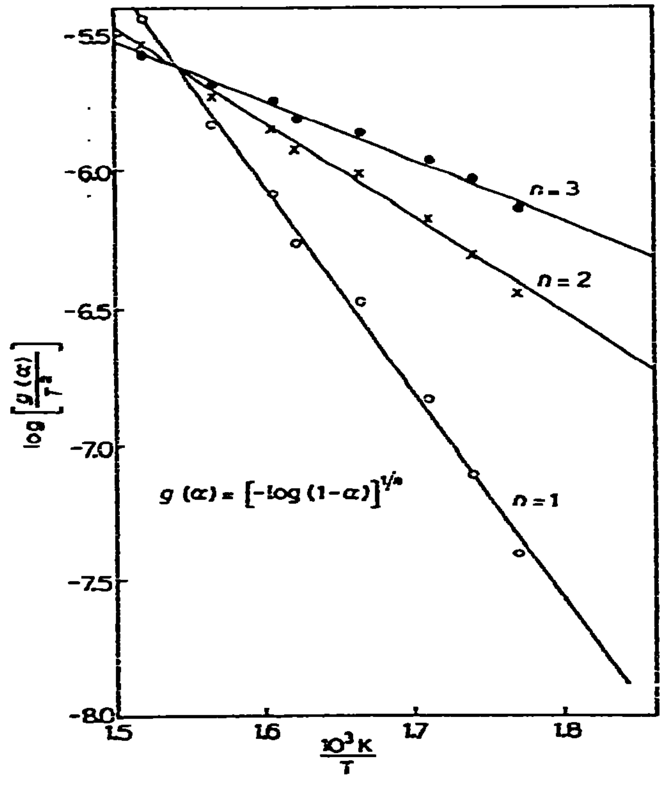

Fig. 2. Plots of log $\left[\frac{\{-\log(1-\alpha)\}^{1/n}}{T^2}\right]$ vs. $\frac{1}{T}$ for the decomposition of $CdCO_3$ in argon.

TABLE 1

THE APPARENT ACTIVATION ENERGY, CORRELATION COEFFICIENT AND LINEAR LEAST SQUARES CONSTANTS[a] *a* AND *b* OF EQN. (1) FOR DIFFERENT VALUES OF *n*

n	*E*(kJ mol^{-1})	*Correlation coefficient*	*a*	*b*
1	143.5 ± 4.2	0.998	− (7.499 ± 0.210)	(5.938 ± 0.347)
2	66.5 ± 4.6	0.997	− (3.487 ± 0.105)	− (0.246 ± 0.174)
3	41.0 ± 1.7	0.997	− (2.150 ± 0.081)	− (2.308 ± 0.118)

[a] $a = -\dfrac{E}{2.3\,R}$; $b = \log \dfrac{ZR}{\beta E}\left[1 - \dfrac{2RT}{E}\right]$.

seen all the three forms of $g(\alpha)$ with $n = 1, 2$ or 3 yielded linear plots with correlation coefficients of almost unity (Table 1). It is therefore not possible to unambiguously determine the correct form of $g(\alpha)$. These results support the theoretical conclusion of Criado and Morales[4].

Using the same apparatus and experimental arrangement, the isothermal decomposition of $CdCO_3$ was followed at 593 ± 1 K which was in the range of non-isothermal decomposition viz., 540–660 K. The isothermal data of α vs. t was also analysed using the equation of Avrami and Erofeyev for $n = 1, 2$ and 3.

$$g(\alpha) = [-\log(1 - \alpha)]^{1/n} = Kt = z.e^{-E'/RT} \tag{3}$$

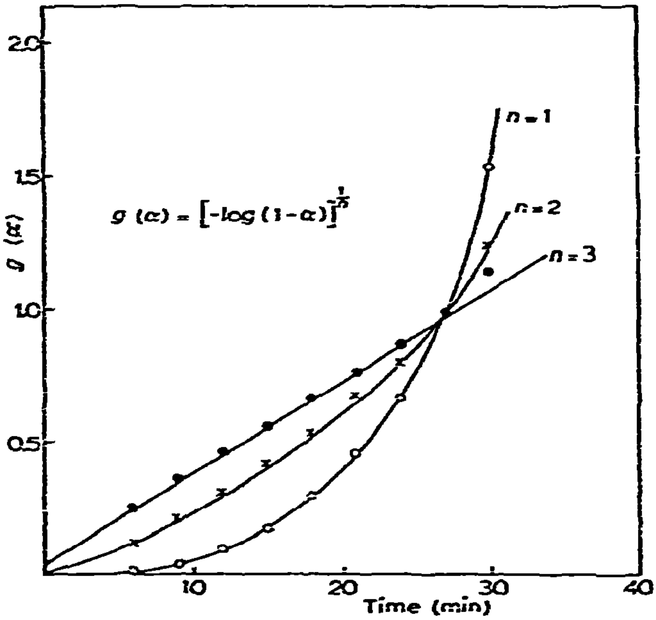

Fig. 3. $g(\alpha)$ vs. time plots for the isothermal decomposition of $CdCO_3$ in argon at 593 ± 1 K.

where K is the specific reaction rate constant and E^1 is the corresponding activation energy of the isothermal process. This analysis yielded a linear plot for $g(\alpha)$ vs. t with the correlation coefficient near unity (0.998) only for $n = 3$. As can be seen for $n = 1$ and 2, non-linear plots were obtained (Fig. 3).

These results therefore underline the necessity of collecting isothermal data for α vs. t for the decomposition reaction in order to choose the proper $g(\alpha)$ function to be used in the analysis of the TG data.

As seen from Fig. 2 and Table 1 each of the linear plots for $n = 1$, 2 or 3 had excellent correlation coefficients. However, the slopes for each of these were quite different, and hence the apparent activation energies calculated had to be different (Table 1) for different values of n. This however is in contradiction to the theoretical deduction made by Criado and Morales[4]. Such dependence of "apparent activation energy" on the value of n is to be expected and in fact was recently reported by Fong and Chen[8] in their study on the decomposition of $Mg(OH)_2$. Similarly Šesták et al.[2] have also observed that the magnitude of the activation energy computed from the TG curves is dependent on the form of $g(\alpha)$ chosen for the data analysis.

In conclusion, the present investigation supports the theoretical analysis of Criado and Morales[4] and emphasizes the necessity for making isothermal measurements before attempting to calculate kinetic parameters from the TG curves. It may be stated that we have in a number of earlier publications[9-12] pointed out the large variations in the values of the kinetic parameters calculated from TG curves and have cautioned about the necessity to carefully evaluate such values. Further investigations on these lines are in progress in our laboratory the details of which will be published elsewhere in the near future.

REFERENCES

1 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand. Sect. A*, 70 (1966) 487.
2 J. Šesták, V. Šatava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 447.
3 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
4 J. M. Criado and J. Morales, *Thermochim. Acta*, 16 (1976) 382.
5 S. R. Dharwadkar, V. V. Deshpande and M. D. Karkhanavala, in I. Buzás (Ed.), *Thermal Analysis*, Akademiai Kiado, Budapest, 1975, Vol. 3, pp. 759–769.
6 M. Avrami, *J. Chem. Phys.*, 9 (1941) 177.
7 B. V. Erofeyev, *C. R. Dokl. Acad. Sci. URSS*, 52 (1946) 511.
8 P. H. Fong and D. T. Y. Chen, *Thermochim. Acta*, 18 (1977) 273.
9 M. D. Karkhanavala and S. G. Rege, *J. Indian Chem. Soc.*, 40 (1963) 459.
10 S. R. Dharwadkar and M. D. Karkhanavala, in R. F. Schwenker Jr. and P. D. Garn (Eds.), *Thermal Analysis*, Academic Press, New York, 1969, Vol. 2, pp. 1049–1069.
11 S. R. Dharwadkar and A. B. Phadnis, *Indian J. Chem.*, 7 (1969) 1032.
12 M. D. Karkhanavala and S. R. Dharwadkar, *Indian J. Chem.*, 7 (1969) 729.