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Note

Possible mis-interpretation of reaction mechanisms from TG data: further discussion

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A recent communication to this journal[1] outlined some of the problems associated with the use of TG curves to determine reaction mechanisms of thermal decompositions. The use of the Coats and Redfern equation[2] in distinguishing between diffusion controlled and phase boundary controlled reactions was discussed and the conclusion was drawn that additional (isothermal) data was required to distinguish properly between two such mechanisms. The purpose of this note is to outline further difficulties arising from reliance on TG curves in deciding on a mechanism.

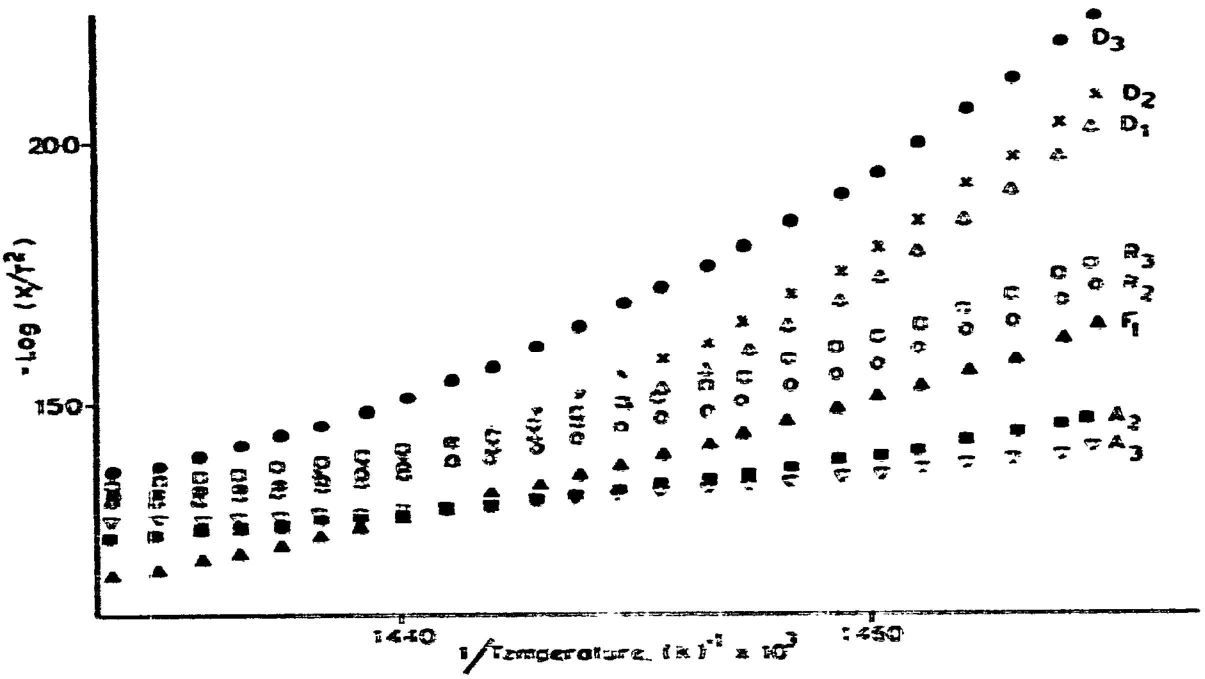
The necessary equations have been derived elsewhere[1, 2] but the important working equation is

$$\log [g(\alpha)/T^2] = \log (AE/R\beta) - \frac{E}{2.3RT}$$

where $g(\alpha)$ is a function depending on the reaction mechanism, E is the activation energy, A the frequency factor, T the absolute temperature and β the heating rate.

The original Coats and Redfern derivation applied only to diffusion controlled reactions, i.e. specific limited forms of $g(\alpha)$, but can easily incorporate a wide range of possible mechanisms to cover phase boundary and nucleation processes[3]. Obviously, plots of $\log[g(\alpha)/T^2]$ vs. $1/T$ should be straight lines of slope $-E/2.3R$. The Arrhenius frequency factor can then be determined from the intercept.

Unfortunately, most discussions of the use of such graphical techniques rarely deal with decomposition reactions about which nothing is known. Most deal with reactions in which some information about the mechanism is known or assumed, i.e. the form of $g(\alpha)$ is known, so that the calculation often involves only the determination of an activation energy. In an experimental situation where, for example, a TG curve has been obtained for a previously unstudied compound, processing of the data through the Coats and Redfern calculation for all possible reaction mechanisms will produce graphs such as those given in Fig. 1, which shows data for the decomposition



of basic lead carbonate[4]. The range of possible mechanisms plotted is one commonly used[3].

Increasingly, therefore, the use of this mathematical treatment to determine mechanisms and Arrhenius parameters is dependent on finding the best straight line in a series. This is the normal "best-fit" technique applied between experimental data and model equation.

It can be seen from Fig. 1 that all the plots are curved; this curvature has been remarked on previously[5, 6]. Statistical data (standard deviations) for the plots are given in Table I. They show that the Avrami-Erofeyev equation with $n = 3$ produces the lowest standard deviation. It therefore follows that naive use of statistical data would suggest a nucleation and growth process as the rate controlling step. Isothermal

TABLE I

CALCULATED STANDARD DEVIATIONS FOR DIFFUSION CONTROLLED DECOMPOSITIONS

Mechanism[a]	*White lead*	*Lead carbonate*[7]	*Laurionite*[8]	*Phosgenite*[9]
D_1	0.04793	0.03547	0.09155	0.06924
D_2	0.04668	0.01784	0.07653	0.06100
D_3	0.04506	0.01793	0.05325	0.04887
D_4	0.04612	0.01193	0.06990	0.05769
F_1	0.02245	0.02345	0.01456	0.01747
A_2	0.01193	0.01168	0.007476	0.008823
A_3	0.008445	0.00776	0.005115	0.00594
R_2	0.02365	0.02653	0.03247	0.02766
R_3	0.02326	0.0254	0.02684	0.02453

[a] Using the nomenclature from Ref. 3

studies show that the decomposition is diffusion controlled[4]. Table 1 also includes data for other diffusion controlled thermal decompositions[7-9], again indicating that the best straight line is given by the Avrami–Erofeyev equations.

It is our belief that the curvature of the Avrami–Erofeyev plots will always be less than that for other models, since the numerical range of $g(\alpha)$ values is much smaller than for others[3].

Diffusion controlled reactions are more susceptible to breakdown of the mathematical boundary conditions; experimental diffusion coefficients and diffusivity may also vary with the extent of reaction. Both of these will give rise to curvature of the plot.

It is for these reasons, in addition to those given by Criado and Morales, that the use of TG curves alone is not to be recommended. The initial determination of a reaction mechanism from isothermal studies removes most of the ambiguities from a TG study and makes possible the determination of Arrhenius parameters much more rapidly than a full isothermal study[10, 11]. Care must be taken, however, to determine isothermal decomposition curves whenever the experimental conditions are changed (e.g. variation in partial pressure of reactant or product gas around the sample), or if wide temperature ranges are studied. Reaction mechanisms must be expected to change in the latter case[12].

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