

THE EFFECT OF PARTICLE SIZE DISTRIBUTION ON TG

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(Received 20 February 1980)

ABSTRACT

The effect of particle size distribution on the fractional reaction has been analysed. The analysis shows that for non-isothermal TG the activation energy and frequency factor evaluated from the fractional reaction by conventional method depend on the particle size distribution, and this may lead to a kinetic compensating effect. Particle size distribution may also lead to an erroneous conclusion about the change in the mechanism of reaction.

INTRODUCTION

TG data is mostly analysed using the integrated form of the rate equation

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \quad (1)$$

to evaluate the activation energy, E , and frequency factor, A , terms of the rate constant, K , as well as the order of reaction, n . In the case of a non-isothermal study, the variation of fractional reaction, α , with temperature, T , can be expressed as

$$\frac{d\alpha}{dT} = A e^{-E/RT} (1 - \alpha)^n \frac{dT}{dt} \quad (2)$$

When dT/dt is a constant, B , Coats and Redfern's [1] integrated form of eqn. (2)

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E}\right) e^{-E/RT} \quad (3)$$

is mostly used to analyse the experimental data. The activation energy and frequency factor of a reaction thus calculated are found to vary over a very wide range. However, $\log A$ and E are found to be linearly related. This effect is termed a kinetic compensating effect [2–4]. Also, activation energy is often found to vary with the rate of heating, B , and in certain cases the plot of $\ln\{g(\alpha)/T^2\}$ vs. $1/T$ shows a break point, indicating a change of reaction mechanism [2,3].

In the present study the validity of eqn. (1) for thermogravimetric studies with non-uniform particle sizes has been analysed.

MATHEMATICAL ANALYSIS

For the purpose of analysis, the decomposition reaction of the type



is considered.

Let us assume that the sample of w g consists of particles of N size fractions, the number of particles of radius R_i being n_i . Assuming that each of these particles is reacting in topochemical fashion and the driving force for the reaction is $c^e - c$, the rate of reaction of the i th size fraction can be expressed as

$$-\frac{d}{dt} (n_i \frac{4}{3} \pi r_i^3 \rho) = 4\pi r_i^2 n_i k (c^e - c) \quad (5)$$

where c^e is the equilibrium concentration of the product gas G , c is the concentration of G in the sample, ρ is the difference in the density of the reactant solid, S , and product solid, S' , r_i is the instantaneous radius of the unreacted core of the particle, and k is the apparent reaction rate constant. Since, in general, thermogravimetric studies are carried out either in vacuum or in an inert atmosphere, eqn. (5) can be simplified to

$$-\frac{d}{dt} (n_i \frac{4}{3} \pi r_i^3 \rho) = 4\pi r_i^2 n_i k c^e \quad (6)$$

The observed rate of reaction is given by

$$-\frac{4}{3} \pi \rho \frac{d}{dt} \sum_{i=1}^N n_i r_i^3 = 4\pi k c^e \sum_{i=1}^N n_i r_i^2 \quad (7)$$

Since with the progress of reaction the finer particles will become completely reacted, the limit of summation in eqn. (7) will vary with time. Denoting $R_i > R_{i-1}$, eqn. (7) can be replaced by its general form

$$-\frac{4}{3} \pi \rho \frac{d}{dt} \sum_{i=1}^{N'} n_i r_i^3 = 4\pi k c^e \sum_{i=1}^{N'} n_i r_i^2, \quad N' \leq N \quad (8)$$

where N' is the number of size fractions that are reacting at any instant and is determined by the condition

$$r_{N'+1} = 0 \quad (9)$$

$$r_{N'} > 0$$

The fractional reaction is given by

$$\alpha = 1 - \frac{\sum_{i=1}^{N'} n_i r_i^3}{\sum_{i=1}^N n_i R_i^3} \quad (10)$$

From eqns. (8) and (10)

$$\frac{d\alpha}{dt} = \left[\frac{3kc^e}{\rho \sum_{i=1}^N n_i R_i^3} \left\{ \frac{\sum_{i=1}^N n_i R_i^3}{\sum_{i=1}^{N'} n_i r_i^3} \right\}^{2/3} \sum_{i=1}^{N'} n_i r_i^2 \right] (1 - \alpha)^{2/3} \quad (11)$$

Comparing eqns. (1) and (11), the rate constant

$$K = \frac{3kc^e}{\rho \sum_{i=1}^N n_i R_i^3} \left\{ \frac{\sum_{i=1}^N n_i R_i^3}{\sum_{i=1}^{N'} n_i r_i^3} \right\}^{2/3} \sum_{i=1}^{N'} n_i r_i^2 \quad (12)$$

If all the particles are of uniform size, i.e., $N = N' = 1$, eqn. (12) simplifies to

$$K = \frac{3kc^e}{\rho R_i} \quad (13)$$

Integrating eqn. (6) with the initial condition, at $t = 0$ $r_i = R_i$; and substituting the resulting expression of r_i in eqn. (12), we have

$$K = \frac{3kc^e}{\rho} \frac{\left(\sum_{i=1}^N n_i R_i^3 \right)^{2/3} \sum_{i=1}^{N'} n_i \left\{ R_i - \frac{kc^e}{\rho} t \right\}^2}{\sum_{i=1}^N n_i R_i^3 \left[\sum_{i=1}^{N'} n_i \left\{ R_i - \frac{kc^e}{\rho} t \right\}^3 \right]^{2/3}} \quad (14)$$

Equations (13) and (14) suggest that if the particles are not of uniform size, the rate constant will depend on the particle size distribution and time.

In the case of a non-isothermal study with constant heating rate, B , eqn. (6) can be expressed as

$$-\frac{dr_i}{dT} = \frac{Z e^{-Q/RT}}{\rho RTB} \left[e^{-(\Delta H^0 - T\Delta S^0)/RT} \right] \quad (15)$$

where Z and Q are the "apparent frequency factor" and "apparent activation energy", respectively, and ΔH^0 and ΔS^0 are the standard enthalpy and entropy changes, respectively of eqn. (4).

Substituting

$$U = \frac{Q + \Delta H^0}{RT} \quad (16)$$

in eqn. (15) and integrating

$$R_i - r_i = -\frac{Z}{\rho RB} e^{\Delta S^0/R} \int_{\infty}^u \frac{e^{-u}}{u} du \quad (17)$$

The values of the integrals on the right-hand side of eqn. (17) can be approximated [5] to

$$-\int_{\alpha}^u \frac{e^{-u}}{u} du = \frac{u^2 + a_1 u + a_2}{u^2 + b_1 u + b_2} \frac{e^{-u}}{u} \quad (18)$$

where, $a_1 = 2.334733$; $a_2 = 0.250621$; $b_1 = 3.330657$; $b_2 = 1.681534$. Using eqns. (10), (17) and (18), the values of α can be evaluated.

RESULTS AND DISCUSSION

The following values were chosen to evaluate the value of α : $\rho = 0.027$ moles cc^{-1} , $Q = 8000$ cal mole^{-1} , $Z = 10^5$ cm h^{-1} , $\Delta H^0 = 40\,200$ cal mole^{-1} , $\Delta S^0 = 34.9$ cal $\text{mole}^{-1} \text{ } ^\circ\text{C}^{-1}$, and weight of the sample = 0.0001 moles. The particle size distribution was assumed to follow

$$R_i = R_{i-1} F \quad (19)$$

$$n_i = n_{i-1} F^{m-3} \quad (20)$$

where F and m are constants. Most of the calculations were carried out with $F = 1/\sqrt{2}$, the factor normally used for particle size analysis.

Figures 1–3 show the calculated values of α plotted as $(1 - \alpha)^n$ vs. time for the isothermal case (Fig. 1) and $\ln\{g(\alpha)/T^2\}$ (eqn. (3)) vs. $1/T$ for the

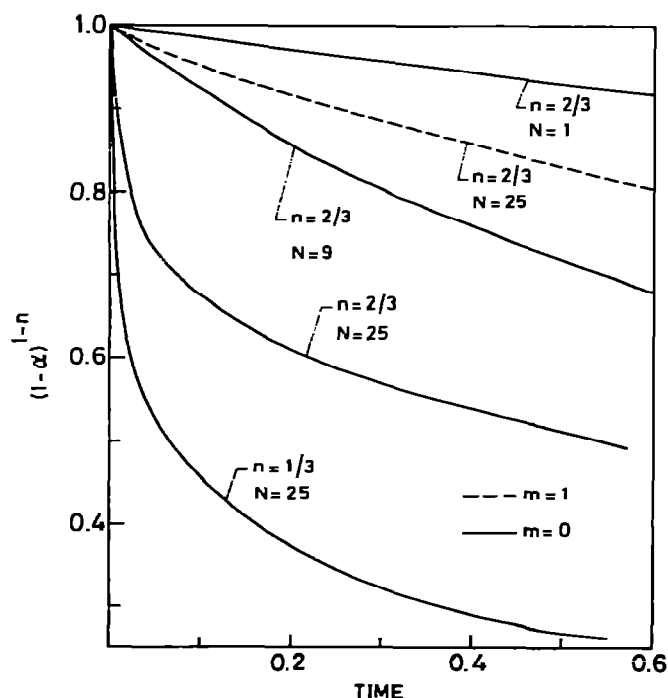


Fig. 1. Effect of particle size distribution on fractional reaction for the isothermal case. $T = 800$ K, $R_1 = 40 \mu\text{m}$, $F = 1/\sqrt{2}$.

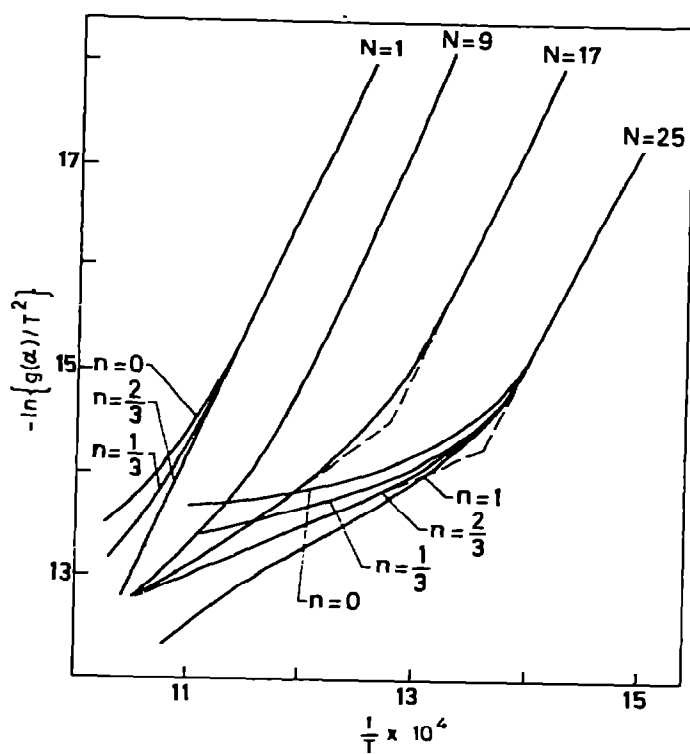


Fig. 2. Effect of particle size distribution on fractional reaction. $m = 0$, $B = 6^\circ\text{C min}^{-1}$, $R_1 = 40 \mu\text{m}$, $F = 1/\sqrt{2}$.

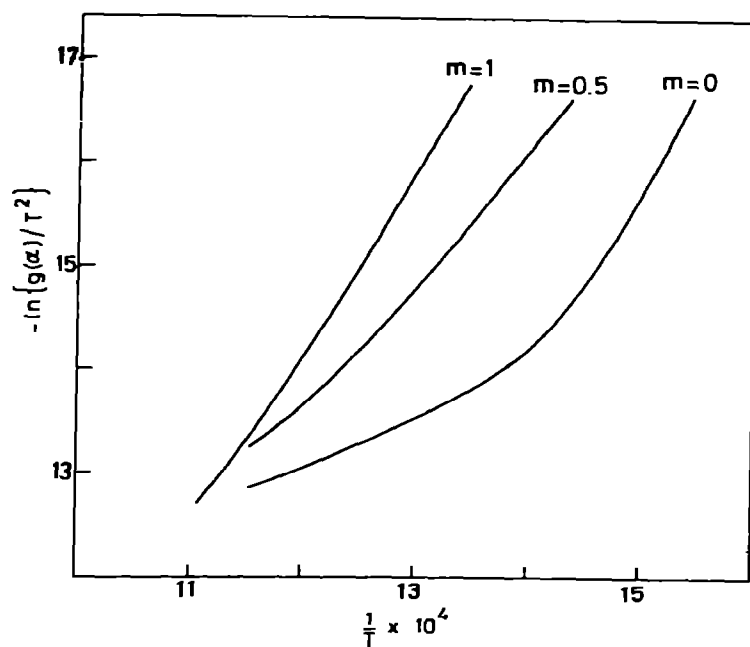


Fig. 3. Effect of particle size distribution on fractional reaction. $N = 25$, $B = 6^\circ\text{C min}^{-1}$, $R_1 = 8 \mu\text{m}$, $F = 1/\sqrt{2}$, $n = 2/3$.

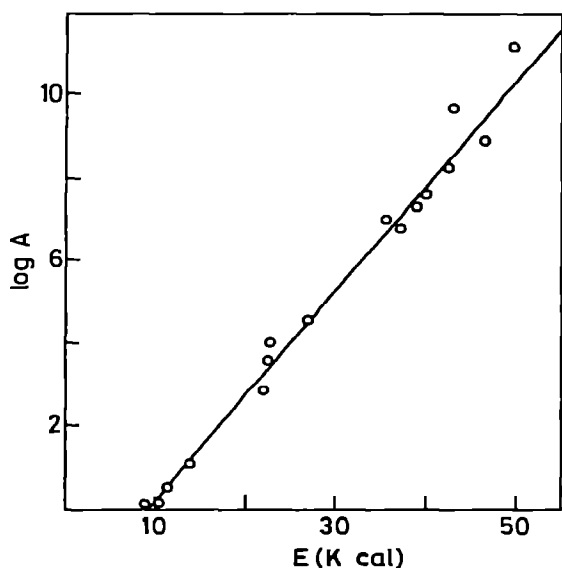


Fig. 4. Kinetic compensating effect.

non-isothermal case. It is apparent that in the case of non-uniform particles the plot may not be linear. The degree of non-linearity depends on the number of size fraction, N (Figs. 1 and 2) and their relative amounts (Figs. 1 and 3), which are determined by the value of m . The value $m = 0$ implies that the relative amounts (weights) of the various size fractions are the same.

If the effect of particle size distribution is not taken into account, the curves for $N = 17$ and 25 in Figs. 1 and 2 may lead to the erroneous conclusion that the mechanism of reaction has changed. Figures 1 and 2 further indicate that the order of reaction, the value of n , is not of much significance for non-uniform particles.

Figure 1 clearly shows that the rate constant (slope of the curve) depends on the particle size distribution. However, calculation of the activation energies from the slope of the approximately linear portion of $(1 - \alpha)^{1/3}$ vs. time plot at different temperatures shows that the activation energy is independent of particle size distribution for the isothermal case. The value of activation energy was found to be the same as the expected value of $48 \text{ kcal mole}^{-1}$.

Figure 4 shows the plot of $\log A$ vs. E obtained from the least square fit of $\ln\{g(\alpha)/T^2\}$ for $n = 2/3$ with $1/T$. In the case of curves similar to that for $N = 17$ and 25 in Fig. 1, to evaluate E and A the curve was approximated to two straight lines, as shown by the dotted line in Fig. 1. An approximately linear relationship between $\log A$ and E suggests that the kinetic compensating effect may be partly due to the particle size distribution.

The calculations with heating rates $B = 3^\circ \text{C min}^{-1}$ and $6^\circ \text{C min}^{-1}$ show that for non-uniform particles E and A evaluated from $\ln\{g(\alpha)/T^2\}$ vs. $1/T$ plot, are slightly dependent on heating rate. The maximum variation of E obtained was about 1 kcal. However, depending on the particle size distribution, increase of heating rate may increase or decrease the activation energy. The present analysis is based on the assumptions that (i) the reaction proceeds from the surface of the particle to its centre in topochemical

fashion, and (ii) the particle size distribution remains unchanged during the progress of reaction.

If each of the fine particles are non-porous, it is expected that the reaction will proceed topochemically. However, if the particles are porous, the reaction can take place throughout its volume [6] and eqn. (5) will not be valid.

During the progress of reaction, the particle size distribution may change due to fragmentation. Although an exact analysis for this case is difficult, it is apparent that the reaction rate, and thereby activation energy, will be influenced by the new particle size distribution.

ACKNOWLEDGEMENT

The author wishes to thank Dr. H.S. Ray for his helpful suggestions and comments.

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