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KINETIC PARAMETERS OF DEHYDRATING IRON OXIDE HYDRATE: DTA AND DTG STUDY

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ABSTRACT

An iron oxide hydrate, $Fe_2O_3 \cdot 1.65\ H_2O$, has been thermally analysed up to 770 K. Two endothermic and one exothermic DTA effects were observed, and two DTG peaks recorded. Analysis of the five peaks was carried out by the methods of Borchardt and Daniels (1957), Piloyan et al. (1966) and Poinsignon et al. (1982). From the three DTA traces, the mean values of activation energy (E_a) and Arrhenius factor (log A) are, respectively: 30.9 and 5.41; 115.1 and 12.20; 219.3 kJ mol^{-1} and 19.22. The first and second dehydration stages in DTG are associated with mean values of E_a and log A equal to: 36.4 and 6.03; 101.9 kJ mol^{-1} and 10.95, respectively. These latter activation energies are in good agreement with values estimated from an F_1-function from dynamic thermogravimetry.

INTRODUCTION

DTA has long been used to investigate and identify endothermic and/or exothermic reactions that take place when a material is heated or cooled. Numerous attempts have been made to widen the scope of DTA application and to define kinetic parameters from its traces. Consequently, many different mathematical expressions have been devised to determine the reaction rate and activation energy, E_a, of solid materials undergoing thermal changes [1–15]. Some expressions correlate the peak temperature with heating rate, while others correlate the heat change on a DTA trace with recorded temperature either by noting ΔT or peak area.

In the present study, the thermal effects of an iron oxide hydrate subjected to thermal analysis were analysed for the purpose of estimating E_a and log A for each of these processes. The kinetic parameters evaluated from DTA and DTG are compared to each other as well as to previous values determined by detailed analysis of the TG curve of the same material [16].

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EXPERIMENTAL

An iron oxide hydrate corresponding to the chemical formula $Fe_2O_3 \cdot 1.65\ H_2O$ [16], was analysed by DTA and DTG techniques. Analysis was carried out with an apparatus produced by Netzsch Gerätebau GmbH Selb, at a heating rate of 5 K min^{-1}.

Procedures for peak analysis

Three analysis procedures were adopted to derive the principal kinetic parameters: activation energy (E_a) and Arrhenius pre-exponential factor (log A).

In the following methods, ΔT denotes the amplitude of the DTA peak at temperature T (K); α_t is the fraction of reactant decomposed at temperature T_t, such that $\alpha_t = a_t/A$; A is the total area of the DTA peak; a_t is the area covered up to T_t; and n is the order of the decomposition (or other) reaction.

1. The method of Borchardt and Daniels (BD)

Their equation describing the first-order decomposition appears in the form [3]

$$K = \frac{\Delta T}{A - a} \qquad (n = 1) \tag{1}$$

where K is the specific reaction constant. A linear relationship should appear upon plotting ln K vs. $1/T$, according to the Arrhenius expressions:

$$K = A\ \exp(-E/RT) \tag{2}$$

and

$$\ln K = \ln(A) - E/RT \tag{3}$$

The values of E_a and log A are easily evaluated from the slope and intercept of the linear plot of eqn. (3).

(2) The methods of Piloyan et al. (Pi)

These authors [5,7] derived an equation applicable to both DTA and TG, without prior determination of the reaction order. Their equation, in the final form appears as

$$\ln \Delta T = C' - n\ \ln(1 - \alpha) - (E/RT) \tag{4}$$

Thereafter, they considered the limited condition of $0.5 > \alpha > 0.4$–0.5, neglected the term $n\ \ln(1 - \alpha)$ and arrived at the expression

$$\ln \Delta T = C' - (E/RT) \tag{5}$$

However, it is inaccurate to neglect the term n ln$(1-\alpha)$ as eqn. (4) could be written as

$$\ln[\Delta T/(1-\alpha)^n] = C - (E/RT) \tag{6}$$

in which the value of $(1-\alpha)^n$ is a function of α and thus will seriously affect the left-hand side of the equation even if a first-order reaction is considered [17].

In practice, plotting of eqn. (5), i.e. ln ΔT vs. $1/T$, is very restricted with a high dispersion of the points. But plotting ln$[\Delta T/(1-\alpha)]$ vs. $1/T$ ($n=1$) yields very satisfactory straight lines in all cases, extending throughout the range $\alpha = 0.1$–0.9 or even beyond.

(3) The method of Poinsignon et al. (PYM)

Their linear equation for the first-order decomposition reaction is [21]

$$\ln[(\mathrm{d}\alpha/\mathrm{d}T)/(1-\alpha)] = \ln(A/\beta) - (E/RT) \tag{7}$$

where β is the linear heating rate. Consequently, the values of E_a and log A are easily derived.

RESULTS AND DISCUSSION

Inspection of the thermal analysis traces in Fig. 1 indicates the presence of three thermal effects in the DTA trace as well as two DTG effects. The three DTA effects appear as two endothermal peaks at 389 and 549 K and an exothermal one at 603 K. The first two endothermal effects are usually ascribed to loss of physically adsorbed water, and dehydroxylation of structural water from iron oxihydroxides. The exothermal effect is attributed by Mackenzie and Berggren [18] and Towe and Bradley [19] to the ready nucleation of the dehydrated residue into α-Fe_2O_3, and the peak represents the final development of α-Fe_2O_3 from the "protohaematite" present before the peak. The same three thermal effects appeared in an iron oxide gel, aged for 155 days at pH 5 [20], but in a much reduced form in comparison to the present material.

Analysis of the five thermal peaks (DTA and DTG) was done by applying the three outlined procedures. The corresponding linear plots are shown in Figs. 2 and 3. The evaluated activation energies and log A values, associated with each process are cited in Table 1.

Comparison of the data indicates that analysis of the first DTA peak (dehydration) by the three methods gives the same value of E_a (30.9 kJ mol^{-1} $\pm$ 4%). Analysis of the corresponding DTG peak gives the somewhat different value of 36.4 kJ mol^{-1} ($\pm$10%) which is about 20% higher than the same value from the DTA curve.

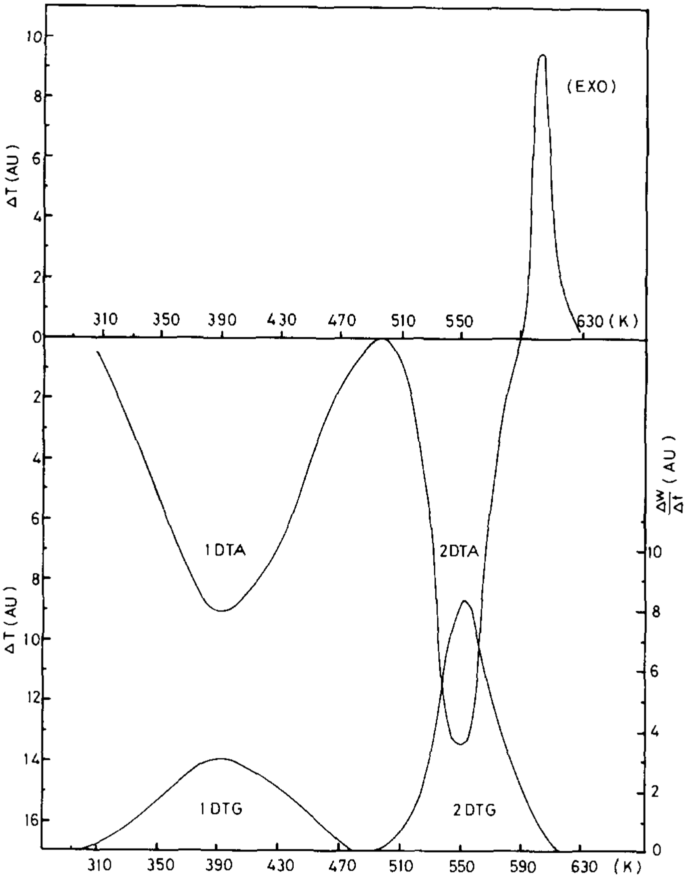

Fig. 1. Thermal analysis of hydrated iron oxide plotted in arbitrary units (AU) of temperature change or differential weight change as a function of temperature.

Analysis of the second DTA peak (dehydroxylation) shows three widely differing values (94–131 kJ mol^{-1}); the lowest is calculated by the PYM method. On the other hand, analysis of the corresponding DTG peak gives values of 93–115 kJ mol^{-1}, the highest value being calculated by the same method (PYM).

The exothermic DTA effect recorded at 578–638 K also gave three slightly differing values of $\overline{E}_a = 219.3$ kJ mol^{-1}.

As mentioned above, all of the applied equations assumed a first-order reaction. To verify this assumption, the order of reaction must be known from an independent method. Thus, the empirical equation suggested by Kissinger [2] was used. This correlates the reaction order, n, to the shape factor of the DTA peak, S by

$$n = 1.26 \times S^{1/2} \tag{8}$$

On applying this relationship, the values of n are found to be 1.16, 1.06 and

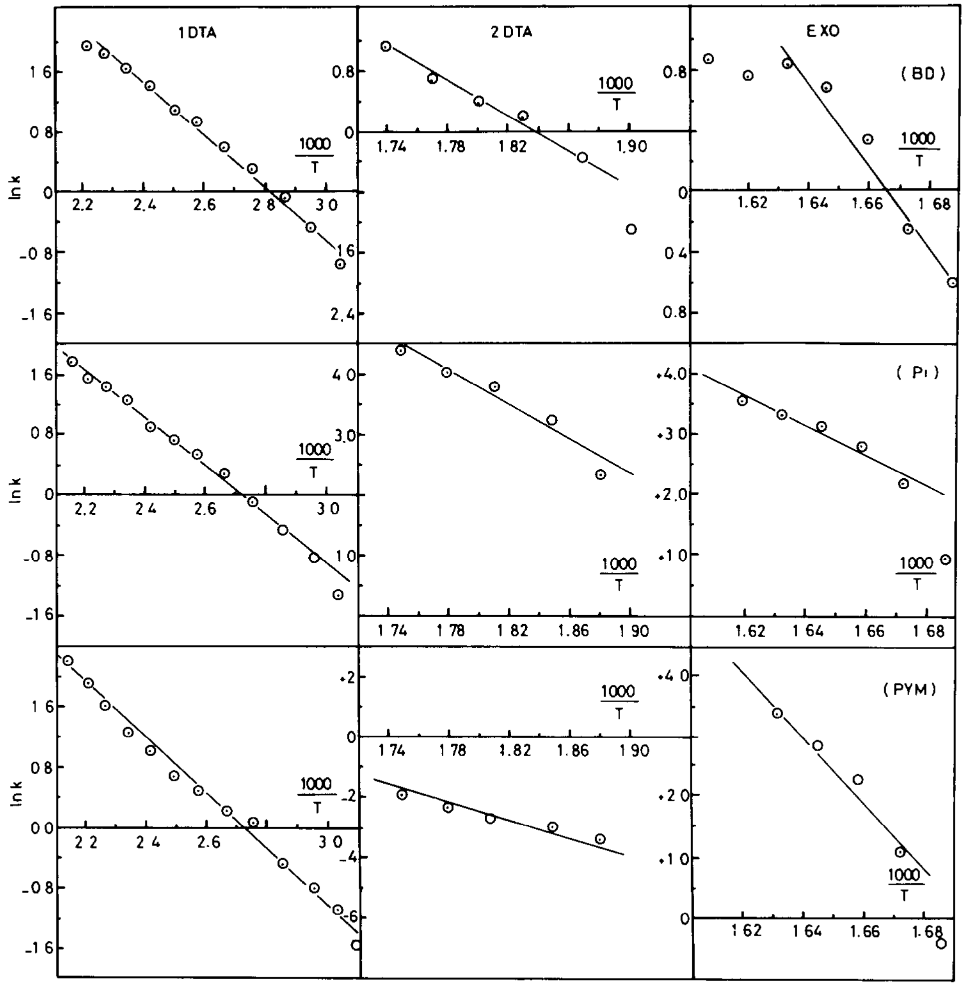

Fig. 2. Linear plots of the BD, Pi and PYM equations for the two endothermal DTA peaks (1DTA, 2DTA) and the exothermal one (EXO).

TABLE 1

Activation energies, E_a (kJ mol^{-1}) and Arrhenius constants, log A, estimated by the three methods of analysis, from DTA and DTG peaks

Process	Peak	BD		Pi		PYM	
		E_a	log A	E_a	log A	E_a	log A
First	DTA	29.8	5.44	32.1	5.34	30.9	5.44
dehydration	DTG	39.7	6.58	35.3	5.82	34.1	5.69
Second	DTA	120.3	12.13	130.8	13.72	94.1	10.75
dehydration	DTG	97.6	10.20	92.8	9.98	115.2	12.66
Exothermic	DTA	211.5	17.52	226.1	20.83	220.3	19.23

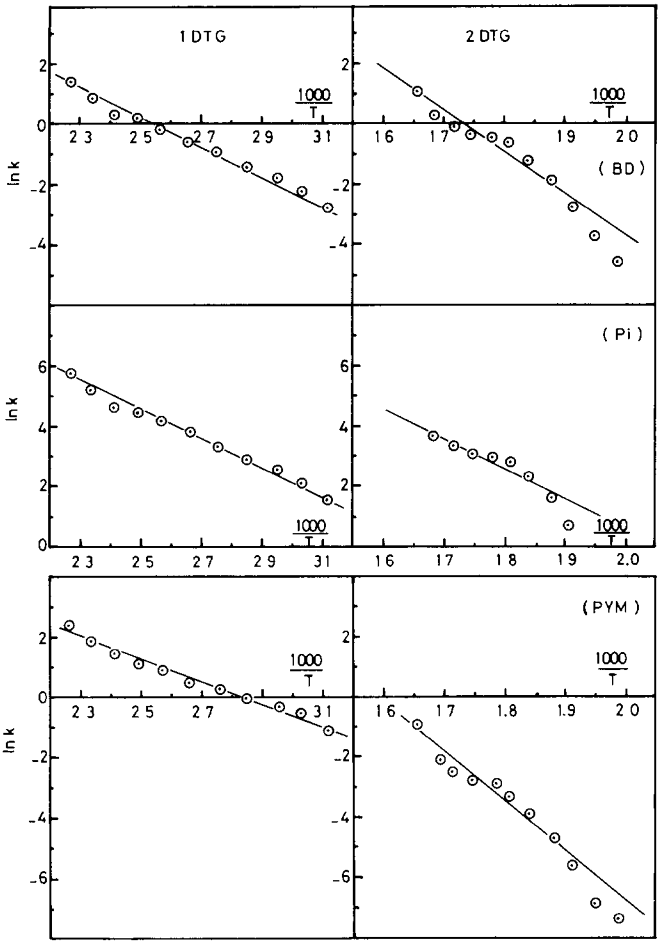

Fig. 3. Linear plots of the BD, Pi and PYM equations for the two DTG peaks of iron oxide hydrate.

1.71 for the three respective thermal effects. This justifies the assumption of a first-order reaction mechanism to describe the dehydration along the DTA endothermal traces. However, the exothermic effect seems to be governed by a higher order reaction mechanism than first order.

In conclusion, analysis of a dynamic thermogram (TG) of iron oxide, and the respective DTG one, although treated by different mathematical expressions, leads to the same activation energy values (i.e. 35.1, 36.4 and 99.4, 101.8 kJ mol^{-1} for the first and second dehydration stages, respectively). This is true when the same decomposition reaction order is assumed to govern in both cases. The derived Arrhenius pre-exponential factors are, however, several orders of magnitude higher when evaluated from the differential curve in comparison to the integral one (6.03, 2.62 and 10.75, 7.0 for the two dehydration steps, respectively).

The three applied methods of analysis, although originally intended to be employed for DTA traces, fit equally well to DTG traces and linearize most of the data ($\alpha = 0.1$–0.9). About 60% of the DTA peaks are linearized by the methods tested.

Finally, dehydration of physically adsorbed water is associated with a low activation energy of about 33 kJ mol^{-1}. Dehydration of structural water in hydrated iron oxide is accompanied by a higher E_a of ~ 107 kJ mol^{-1}. The exothermic transformation to the stable α-Fe_2O_3 needs a higher energy (~ 200 kJ mol^{-1}) and shows a high pre-exponential factor ($\log A = 18.5$).

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