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DECOMPOSITION KINETICS OF MAGNESIUM HYDROXIDE USING DTA

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ABSTRACT

The decomposition kinetics of magnesium hydroxide to magnesium oxide have been followed using differential thermal analysis (DTA). The method of determining the ideal conditions for calculating the decomposition kinetics is described. For the decomposition the kinetic equation describing the process is found to be

$$\frac{d\alpha}{dT} = (1-\alpha)^{4/3}\left[(1-\alpha)^{1/3}-1\right]$$

Values of activation energies were found to be from 229 to 88.3 kJ mol^{-1}.

INTRODUCTION

A number of attempts have been made to define kinetic parameters by differential thermal analysis (DTA) [1–4]. Each of the suggested procedures is based on the assumption that the rate of heat absorption or evolution during a reaction is proportional to the rate of that reaction at the temperature at which it is measured. A number of different methods have been devised to determine the rate of heat change in a sample.

The first use of DTA in the study of kinetics was made by Murray and White [5]. They studied the decomposition of kaolin and observed the effect of heating rate on the temperature of the peak. Kissinger [1} assumed that the thermal properties of the reacting mass in a DTA cell could be standardized and that the rate of heat change could be directly reflected as a change in temperature within the sample, correlating the temperature at which the maximum DTA deflection occurred with the rate of heating of the sample.

Although Kissinger's approach for analyzing data from DTA current was criticized by Reed et al. [6], and Melling and Mackenzie [7] to be invalid in a practical experiment, Akita and Kase [8] have shown it to be valid provided that appropriate experimental conditions such as small cell dimensions, slow heating rate, and moderate reactions of sample materials are used. Akita and Kase [8] concluded that the peak maximum (T_m) of the DTA curve was at the maximum reaction rate and thus agreed with Kissinger's findings, thereby placing the Kissinger relationship on a more sound theoretical basis.

Olafsson and Bryan [9] have developed the Kissinger method for the determination of the procedural activation energy, E_a, in terms of the T_m values and the heating rate, for thermal decomposition of crystalline amino acids. The procedure employed by the investigators are complicated in that (a) it required the determination of several DTA curves of different heating rates and (b) it needed a minimum of three Gaussian distributions to be resolved from the DTA curves by a sophisticated curve-resolver. Thus, three similar or equivalent E_a values were generally obtained from three correspondingly resolved peaks of an original single endothermic peak of a DTA curve.

Undoubtedly the most important theory developed to obtain kinetic parameters from DTA results is that of Borchardt and Daniels [10]. A review by Sharp [11] gives theoretical objections to the method of Kissinger, which has been shown to be incorrect [10]. The methods of Piloyan et al. [4] and Reich [3] have been criticized on theoretical grounds by Melling and Mackenzie [7]. The most satisfactory method which was found by Sharp [11] and Girgis [12] was due to Borchardt and Daniels, where the authors described their equation for systems involving stirred solutions and specifically warned against their use in solid-state reactions.

The methods of investigating reaction kinetics by DTA were reviewed by Satava [13], Sestak and Berggren [14] and Sharp [11].

The mathematical proof of the method has been given by other authors [15]. Before the method can be used experimentally, there are many conditions which have to be met. Davies et al. [15] have discussed them in detail.

EXPERIMENTAL

In the present investigation, it was decided to carefully establish experimental conditions which were the most favorable to the determination of kinetics from DTA data.

All the DTA experiments were carried out using the Stanton-Redcroft 673-4 differential thermal analyzer. The instrument covers a temperature range from ambient to 1273 K, and variable heating rates from 1.0 to 100 °C min^{-1}. A Pt/Pt–13%Rh thermocouple assembly was used with a high gain, low noise, low drift DC amplifier for temperature measurement and control.

A series of DTA experiments on magnesium hydroxides ($Mg(OH)_2$) were performed in flowing dry air. It was found that the DTA curve could not be reproduced accurately, as it was difficult to accurately control the air flow rate. It was decided to perform the experiments in still air, when it was possible to accurately produce a DTA curve on any one sample and to show that it was reproduced accurately in repeated experiments performed over a period of several weeks.

Another problem with the quantitative DTA experiments arose from the baseline shift. The baseline shift not only makes calculation of peak areas difficult and less accurate but also indicated the difference between the specific heat capacity of the sample and that of the reference. A flat, horizontal baseline, therefore, would give the most advantageous condition possible in the determination of reaction kinetics.

A series of DTA experiments were made on a single $Mg(OH)_2$ sample with "dead burnt" alumina as reference standard. In these experiments it was found that silica crucibles gave better results than the more normal platinum crucibles. Having established the need to change the crucibles, it was then decided to vary the sample and reference weights, until a flat baseline was obtained.

A typical DTA curve is shown in Fig. 1 and the relationship between temperature (or time) and change in enthalpy is noted. For the endothermic decomposition of $Mg(OH)_2$, the decrease in enthalpy of the sample equals the heat absorbed during the decomposition plus the heat transferred to the holder from the surroundings.

If the conditions mentioned by Sharp [11] are fulfilled, it is possible to estimate graphically from the DTA curve all the values necessary for substitution into the equations. Only the reaction order remains unknown and that can be determined by a suitable computer program.

Two samples of magnesium hydroxide were chosen for the initial study. One was bought from BDH as a normal reagent grade hydroxide and the second sample was supplied by Steetley Seawater Magnesias, made by their seawater process. Both the samples were characterized by X-ray fluorescence (XRF) spectroscopy before and after the decomposition. The results are

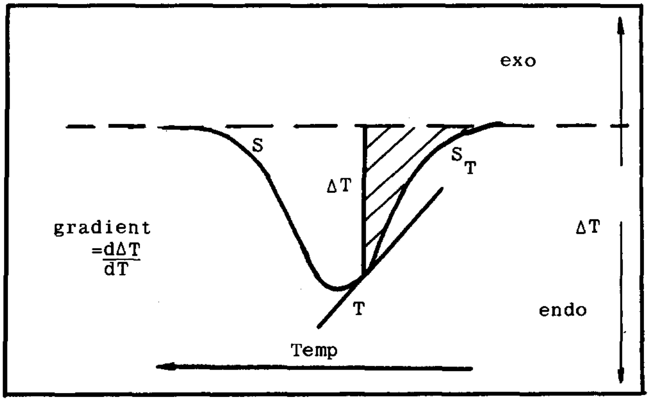

Fig. 1. A typical DTA endotherm.

TABLE 1

XRF analysis of magnesium hydroxides

	Sample A	Sample B
CaO	1.60	0.97
SiO	0.32	0.02
Fe_2O_3	0.11	0.05
Al_2O_3	0.05	–
Cr_2O_3	0.007	0.006
Mn	0.0211	0.0042
MgO	69.52	69.46

TABLE 2

Experimental conditions for DTA analyses

Reference material	"Dead" burnt alumina
Heating rates (°C min^{-1})	10, 15, 20
Atmosphere	Static air
Sample holder	Fused silica
Thermocouple	Chromel–alumel
Temperature range	Ambient–1000°C
Sample weight	0.25 g

given in Table 1. Both the samples were analyzed under identical conditions (Table 2).

DETERMINATION OF REACTION KINETICS

The fraction, α, decomposed at temperature, T, is the ratio of the peak area at temperature T compared to the total peak area. The rate of decomposition with respect to time is given by

$$\frac{d\alpha}{dt} = K f(\alpha) \tag{1}$$

where K is the rate constant and $f(\alpha)$ depends on the reaction mechanism. Also

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\frac{dt}{dT} = \frac{K[f(\alpha)]}{\beta} \tag{2}$$

Where

$$\frac{dt}{dT} = \beta, \text{ the heating rate} \tag{3}$$

It is then possible to analyze the data using the Arrhenius equation

$$K = A \exp(-E/RT) \tag{4}$$

in the same manner as data collected from a series of isothermal plots.

Substituting the Arrhenius into eqn. (2)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = \frac{\mathrm{f}(\alpha) A \exp(-E/RT)}{\beta} \tag{5}$$

$$\frac{\dfrac{\mathrm{d}\alpha}{\mathrm{d}\tau}}{\mathrm{f}(\alpha)} = \frac{A}{\beta}\exp(-E/RT) \tag{6}$$

$$\ln\frac{\mathrm{d}\alpha/\mathrm{d}\tau}{\mathrm{f}(\alpha)} = \ln\frac{A}{\beta} - \frac{E}{RT} \tag{7}$$

The above equation was originally developed by Achar [16] and later used by other workers [17] for application to thermogravimetry. By plotting $\ln[(\mathrm{d}\alpha/\mathrm{d}\tau)/\mathrm{f}(\alpha)]$ vs. $1/T$, A and E may be calculated provided the form of $\mathrm{f}(\alpha)$ is known, i.e., the gradient will be E/R and the intercept $\ln(A/B)$. The values of $\mathrm{d}\alpha/\mathrm{d}t$ are the tangents to the curve of α vs. T and α is derived from (see Fig. 1)

$$\alpha = \frac{S_T}{S} \tag{8}$$

The function $\mathrm{f}(\alpha)$ was established from the differential form of the standard rate equations given in Table 3.

By developing computer programs, it was possible to construct plots of α vs. T, of the form shown in Fig. 2. In another computer program, eqn. (7)

TABLE 3

Kinetic expressions tested for the rising temperature decomposition

Equation No.	$\mathrm{f}(\alpha)$ (differential form $\frac{\mathrm{d}\alpha}{\mathrm{d}t} =$)	Equation No.	$\mathrm{f}(\alpha)$ (differential form $\frac{\mathrm{d}\alpha}{\mathrm{d}t} =$)
1	α^{-1}	12	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
2	$[-\ln(1-\alpha)]^{-1}$	13	$(1+\alpha)^{1/2}[(1+\alpha)^{1/2}-1]^{-1}$
3	$[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$	14	$[(1-\alpha)^{-1/3}-1]^{-1}$
4	1	15	$(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$
5	$(1-\alpha)$	16	$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{1/2}$
6	$(1-\alpha)^{1/2}$	17	$(1-\alpha)^{2/3}[(1-\alpha)^{1/3}]^{2/3}$
7	$(1-\alpha)^{2/3}$	18	$\alpha^{1/2}$
8	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	19	$\alpha^{2/3}$
9	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	20	$\alpha^{3/4}$
10	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	21	$(1-\alpha)^{1/3}$
11	$(1-\alpha)[-\ln(1-\alpha)]^{1/4}$	22	$(1-\alpha)^{-2}$

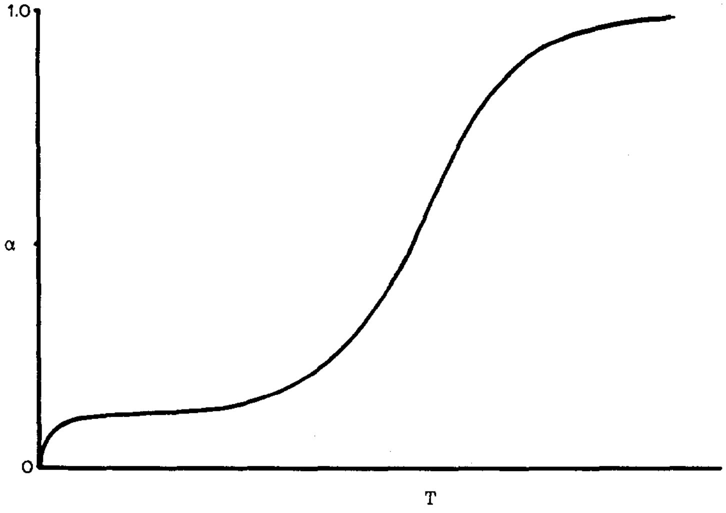

Fig. 2. A typical plot of α vs. T.

was solved using a series of rate equations for f(α) given in Table 3. The correct rate equation was determined as that which gave the best straight-line fit. For each sample the values of ln K and $1/T$ were calculated and a plot of ln K vs. $1/T$ was constructed. A typical plot for each of the samples is given in Figs. 3 and 4 by visually assuming the ln K vs. $1/T$ plots. It was possible to select a range of α values which gave a straight line, as indicated in Figs. 2 and 3. The values of ln K and $1/T$ could then be found from within the selected α range. The straight line was analyzed using the method of least

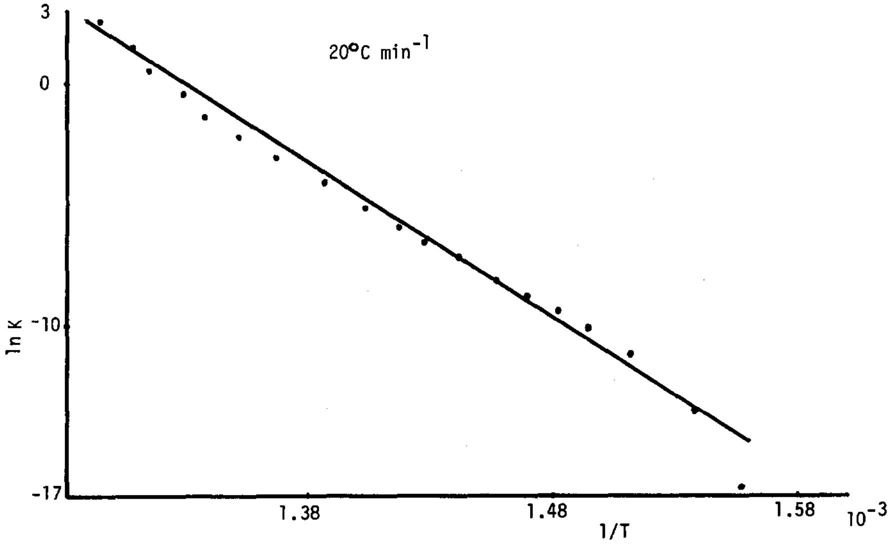

Fig. 3. A typical plot of ln K vs. $1/T$.

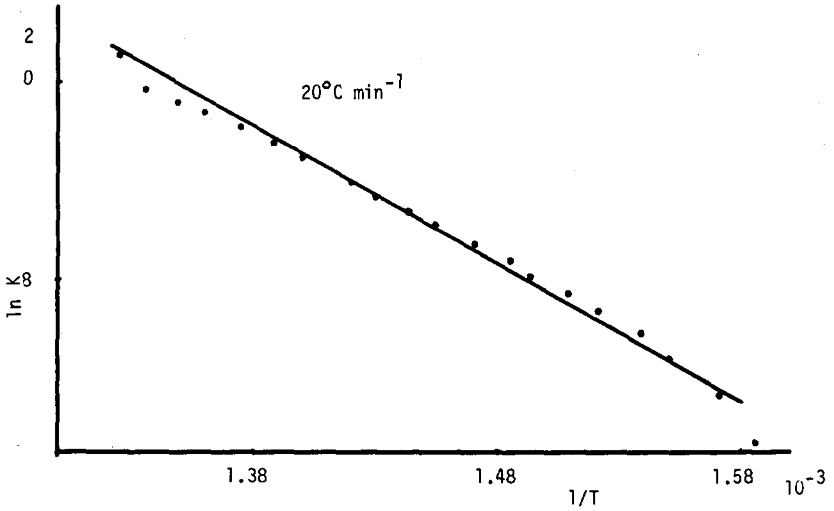

Fig. 4. A typical plot of ln K vs. $1/T$.

squares to determine the slope (E/R), the intercept (ln A) and the correlation coefficient for the line as in eqn. (7). The results are shown in Table 4.

The variation in activation energy calculated using the equation given in Table 4 was large (viz. eqns. 4, 8, 15 and 22) and this is clearly seen in Table 4. The results from DTA experiments were usually described by equation 15, i.e.

$$(1-\alpha)^{4/3}\left[(1-\alpha)^{1/3}-1\right]^{-1}=\frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

$$\left\{\left[1/(1-\alpha)^{1/3}\right]-1\right\}^{2}=Kt$$

the Zhurovlev equation was used in the differential form. The results from eqn. (15) gave an activation energy of 222.5 kJ mol^{-1}, and if in fact just one

TABLE 4

Results obtained from the two samples of magnesium hydroxide studied

Equation No.	Heating rate (°C min^{-1})	Activation energy (kJ mol^{-1})	Pre-exp. factor (s^{-1})
Sample A			
15	20	207.8	74.1
15	15	207.8	70.88
15	10	198.9	69.88
Sample B			
5	20	103.5	80.6
8	15	88.3	1.36×10^{-1}
5	10	229.5	75.8

expression was used (eqn. 15) sensible results were possible. This method can be used to investigate one series of samples and detect any variation in activation energy.

With respect to the decomposition kinetics, it has been shown that DTA offers a suitable method for determining the mechanism of a reaction which does not involve a weight change or change in physical state—parameters that afford the classical isothermal approach of determining reaction kinetics. The arithmetical errors and the time consuming approach of linear regression analysis to determine the correct mechanism have been eliminated by the use of computer programs.

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