

THERMAL DECOMPOSITION KINETICS OF SOLIDS FROM DDTA CURVES

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ABSTRACT

It is shown that the activation energy for solid thermal decompositions which follow a first order kinetic equation can be determined in a very simple manner from a single derivative differential thermal analysis (DDTA) curve. The experimental results are in good agreement with those obtained by other workers.

INTRODUCTION

Thermoanalytical methods such as differential thermal analysis (DTA) and thermogravimetry (TG) are extensively used in investigations on solid state reactions; these techniques involve continuous measurements of changes in a physical property such as weight, heat capacity or enthalpy, as the sample temperature is increased at constant heating rate.

The advantages of evaluating reaction kinetics by a continuous increase in sample temperature are that considerably less experimental measurements are required than in the isothermal method, a temperature range can be covered continuously without any gaps using a very small amount of sample.

The several methods [1–8] proposed for obtaining kinetic data from DTA curves are based on two procedures. In the first, the peak temperatures are detected on DTA curves recorded at several different heating rates [1–5]; in the second, the heights and/or the areas under a single DTA peak are measured [6–8]. As the peak temperatures are the most reproducible and easy to detect data on a DTA curve, the former procedure leads to more reliable results.

In this paper a new method based on the measurements of two peak temperatures on a single derivative differential thermal analysis (DDTA) curve for determining the activation energy of the thermal decomposition of solids is described.

EXPERIMENTAL

A Netzsch 404 M thermoanalyzer was used for DTA investigations. The DTA apparatus comprised of a vertical furnace and calibrated PtRh 10%–Pt thermocouples. Programmed heating of the furnace was assured by a Netzsch 411 temperature programmer. Temperature against time (T/t), differential temperature against time ($\Delta T/t$) and its first derivative were simultaneously recorded by a strip-chart recorder. NaHCO_3 and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (BDH AnalaR) were used. Alumina (E. Merck chromatographic grade) was used both as the diluent and reference material. Ten mg of powdered (< 300 mesh) sample were gently packed in a Pt sample holder between two layers of alumina. Differential thermal analysis curves in air at a heating rate of $10^\circ\text{C min}^{-1}$ were recorded.

THEORY AND RESULTS

Most thermal decompositions of solids involve reactions of the type



This process takes place in several stages, i.e. the chemical act of breaking of bonds, destruction of the initial crystal lattice, formation of the crystal lattice of the solid B, absorption–desorption of the gaseous products, diffusion of gas, heat transfer.

The rate of the thermal decomposition is determined by the rate of one or more of these stages. Sometimes the rate-determining step changes during the process.

The process governed by a unitary kinetic law can be described by

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

where α is the volume fraction reacted at time t , and n is the reaction order. The constant k is related to the absolute temperature by an Arrhenius type equation

$$k = A \exp(-E/RT) \quad (2)$$

where E is the activation energy and A is a constant.

As the thermal decomposition proceeds, the heat of decomposition is absorbed and an endothermic peak appears on the DTA curve (Fig. 1). Since small amounts of sample and reference material in identical holders are used and the sample is diluted with the reference material, it may be assumed that (a) the temperature within the two holders is uniform; and (b) the heat transfer coefficient K and the heat capacities C_p of the sample and the reference material are the same.

The heat balance during a time period dt in the DTA process can be approximately expressed by [6]

$$d(\Delta H) = C_p d(\Delta T) + K \Delta T dt \quad (3)$$

where ΔT is the temperature difference between the sample and the reference

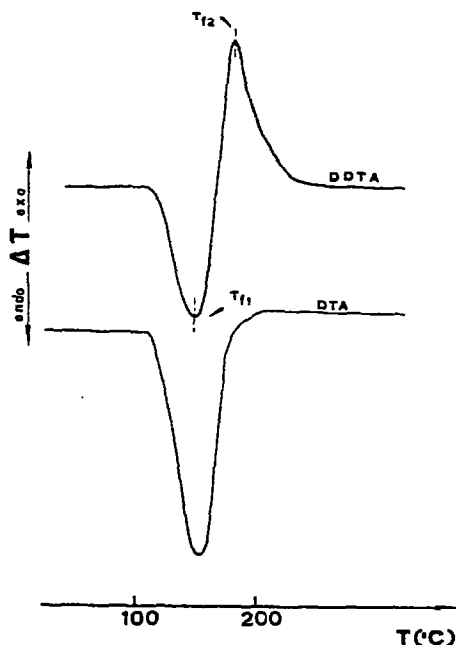


Fig. 1. DTA and DDTA curves of the thermal decomposition of NaHCO_3 .

material, and ΔH is the amount of heat associated with the reaction.

Assuming C_p and K to be independent of the temperature over the reaction period, the following expression can be derived

$$\Delta H = C_p \int_{t_1}^{t_2} d(\Delta T) + K \int_{t_1}^{t_2} \Delta T dt \quad (4)$$

Since ΔT is zero at both $t = t_1$ and $t = t_2$, the first term of the right-hand side of eqn. (4) is zero.

The integral in the second term of eqn. (4) is the total area S under the peak. Therefore

$$\Delta H = KS \quad (5)$$

Substituting the relation $\alpha = d(\Delta H)/\Delta H$ and eqn. (5) in eqn. (3) we obtain

$$\frac{d\alpha}{dt} = \frac{1}{KS} \left[C_p \frac{d(\Delta T)}{dt} + K \Delta T \right] \quad (6)$$

As $C_p d(\Delta T)/dt$ is an order of magnitude smaller than $K\Delta T$, eqn. (6) can be

approximated as [6]

$$\Delta T = S \frac{d\alpha}{dt} \quad (7)$$

The temperature T_i at the inflection points, i.e. at the minimum and maximum slope of the DTA peak, can be obtained by setting

$$\frac{d^2\Delta T}{dt^2} = \frac{d^3\alpha}{dt^3} = 0 \quad (8)$$

and solving for T_i .

For a process governed by a first order equation ($n=1$), eqn. (8) is satisfied if

$$\frac{d^2k}{dt^2} - 3 \frac{dk}{dt} k + k^3 = 0 \quad (9)$$

The first time derivative of the rate constant k is

$$\frac{dk}{dt} = \frac{dT}{dt} \frac{dk}{dT} = \beta \frac{E}{RT^2} k \quad (10)$$

As $E/RT_i \gg 2$ [4], the second time derivative of k is

$$\frac{d^2k}{dt^2} \approx \left(\beta \frac{E}{RT^2} \right)^2 k \quad (11)$$

where β is the DTA heating rate.

Putting eqns. (10) and (11) into eqn. (9) gives

$$\left(\frac{k}{a} \right)^2 - 3 \left(\frac{k}{a} \right) + 1 = 0 \quad (12)$$

where $a = \beta E / RT_i^2$.

Two solutions of eqn. (12) exist which correspond to the two inflection points f_1 and f_2 of the DTA peak and their ratio is expressed by

$$\left(\frac{k}{a} \right)_{f_2} / \left(\frac{k}{a} \right)_{f_1} = 6.85 \quad (13)$$

Taking into account eqn. (2) the logarithms of eqn. (13) lead to

$$\frac{E}{R} \left(\frac{1}{T_{f_1}} - \frac{1}{T_{f_2}} \right) = 1.92 - \ln \left(\frac{T_{f_2}}{T_{f_1}} \right)^2 \quad (14)$$

As the ratio T_{f_2}/T_{f_1} is very close to unity, dropping the second term of the right-hand side of eqn. (14) gives the activation energy as

$$E = \frac{1.92 R}{1/T_{f_1} - 1/T_{f_2}} \quad (15)$$

The two inflection point temperatures correspond to the temperatures of the double peak on the DDTA curve in Fig. 1.

TABLE I

Kinetic results by DTA methods

Reaction	Source of data	E (kJ mole ⁻¹)
$2 \text{ NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$	Present work	90
	Wendlandt [9]	84
	Reich [10]	92–100
	Subramanian [11]	80– 96
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	Present work	99
	Wendlandt [9]	113
	Piloyan et al. [7]	88
	Skvara and Satava [8]	92

To illustrate the above method the decomposition of NaHCO_3 and the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, which follow a first order rate equation [8–11], were studied. The activation energy values for the reactions calculated using eqn. (15) from the inflection point temperatures are reported in Table I and compared with those obtained by other workers who have used alternative DTA methods. The very good agreement between the data of the present work and the literature data proves the validity of the method.

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