

# Measurements of Kinetic Constants by the Differential Thermal Analysis

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## Abstract

Many methods for measuring kinetic constants of decomposition reaction by the differential thermal analysis (DTA) have been proposed, but no method for determining the order of reaction, activation energy and frequency factor concurrently has been proposed. In the present paper, the kinetic constants of decomposition reaction are determined concurrently by DTA using the variation of peak temperature with heating rate on differential thermal curve. The present and the previous methods were applied to the dehydration of magnesium hydroxide. The values obtained by the both methods agreed well with each other.

## 1 Introduction

Prototype of DTA was constructed for the study of clay by Le Chatelier in 1887, and DTA has been universally accepted by mineralogical laboratories as a rapid and convenient means for recording the thermal effects that occur as a sample is heated.

There have been many works in which DTA was used for the study of the kinetics of the reaction. Koderu, Kusunoki and Shimizu<sup>1)</sup> measured the change in the free energy of decomposition reaction of CuO by DTA measurement under the different pressures. The methods of measurements of kinetic constants which are different from the DTA measurement by them and carried out by the normal DTA technique have been proposed by Kissinger<sup>2)</sup>, Toop<sup>3)</sup> and others.

Kissinger assumed that there is the peak temperature when the reaction rate is maximum and calculated the activation energy from the variation of peak temperature with heating rate. This assumption was supported by Murray and White<sup>4)</sup>. They reported that the kinetic constants and the heating rate determined the temperature of the maximum deflection of DTA curve.

On the other hand, Tsuzuki and Nagasawa<sup>5)</sup> pointed out that the shape of DTA curve is determined not only by the change of the reaction rate during linear heating but also by that of the temperature distribution in the sample and analyzed the shape of DTA curve. They found the fact that the peak temperature was somewhat higher than the temperature at which decomposition proceeds most rapidly.

Toop considered that after the reaction the DTA curve changes exponentially with time and the area of peak formed by shifting this exponential curve is proportional to the fraction of reactions. Then, Toop derived the relation between the fraction of reactions and the temperature from DTA curves and applied this method to the thermal endurance test of insulator.

Kissinger and Toop measured the activation energy of decomposition reaction assuming that the reaction was the first-order law.

However, no method for determining the order of reaction, activation energy and frequency factor of decomposition reactions concurrently by the DTA technique has been proposed. In the present paper, an equation is derived for the concurrent determination of kinetic constants. The present method was tested for the dehydration of magnesium hydroxide and the obtained values of kinetic constants were compared with those by the previous methods.

## 2 Theory

### 2.1 Outline of Previous Methods

#### 2.1.1 The Kissinger's Method

The decomposition reaction obeys the first-order law. Hence, at constant temperature,

$$\left(\frac{\partial x}{\partial t}\right)_T = K_T(1-x), \quad (1)$$

where  $x$  is the fraction of decomposed material and  $K_T$  the kinetic constant in the Arrhenius equation. When the temperature is the function of time, the reaction rate is expressed as

$$\frac{dx}{dt} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t \frac{dT}{dt}. \quad (2)$$

The rate of change of  $x$  with temperature, with the time coordinate fixed,  $(\partial x/\partial T)_t$  is zero. The only effect of an instantaneous change in temperature is in the velocity of thermal motion of the particles. Then, the total rate of reaction may be expressed as

$$\frac{dx}{dt} = A(1-x) e^{-E/RT}, \quad (3)$$

where  $A$ ,  $E$  and  $R$  are the frequency factor, the activation energy and the gas constant, respectively.

When the reaction rate is a maximum, its derivative with respect to time is zero. Differentiating Eq. (3) with respect to  $t$ , we get

$$\frac{d}{dt} \left( \frac{dx}{dt} \right) = \frac{dx}{dt} \left( \frac{E}{RT^2} \frac{dT}{dt} - A e^{-E/RT} \right). \quad (4)$$

The maximum value of  $dx/dt$  occurs at temperature  $T_m$ , defined by

$$A e^{-E/RT_m} = \frac{E}{RT_m^2} \frac{dT}{dt}. \quad (5)$$

Eq. (5) becomes

$$\frac{d \left( \ln \frac{\phi}{T_m^2} \right)}{d \left( \frac{1}{T_m} \right)} = - \frac{E}{R}, \quad (6)$$

where  $\phi = dT/dt$ , the heating rate. The activation energy is determined from the slope by plotting  $\ln(\phi/T_m^2)$  against  $1/T_m$ .

### 2.1.2 The Toop's Method

It can be argued that the rate of heat generated in the cell is equal to the rate of accumulation of heat in the sample plus the rate of heat loss or

$$\frac{dq}{dt} = ms \frac{dh}{dt} + Bh, \quad (7)$$

where  $q$  is the instantaneous heat generated,  $m$  the mass of the sample,  $s$  specific heat,  $h$  the exotherm or endotherm and  $B$  Newton's cooling constant for the cell. Integrating Eq. (7) from  $t=0$  to some instantaneous value, we find that

$$\int_0^q dq = msh + B \int_0^t h dt. \quad (8)$$

Using the heating rate, that is,

$$\frac{dT}{dt} = \phi = \text{constant} \quad (9)$$

and integrating Eq. (8), we get

$$q = msh + \frac{B}{\phi} \int_0^T h dT. \quad (10)$$

At this stage, since for every mole of chemical bond broken or rearranged, there is a definite quantity of heat evolved,  $q$  can be related to the extent of degradation  $(1-r)$

$$q = mC(1-r), \quad (11)$$

where  $C$  is the total heat of reaction per unit mass of sample. Eliminating  $q$  from Eqs. (10) and (11) gives

$$h = -\frac{B}{ms\phi} \int_0^T h dT + (1-r) \frac{C}{s}. \quad (12)$$

Exotherms are normally recorded as thermocouple voltage  $v$ , that is,

$$v = \lambda h, \quad (13)$$

where  $\lambda$  is the thermoelectric EMF (V/°C). Thus, we get

$$v = -\frac{B}{ms\phi} \int_0^T v dT + (1-r) \frac{C\lambda}{s}. \quad (14a)$$

If thermograms are integrated numerically and  $v$  plotted against  $\int v dT$ , Eq. (14a) will show a straight line of slope  $B/ms\phi$  where  $r$  becomes zero. Moreover, the intercept will be equal to  $C\lambda/s$ .

The general equation of a thermogram is

$$g(r) - g(r_0) = \frac{AE}{\phi R} p(y), \quad (15)$$

where

- $g$  general integrated order function,
- $A$  Arrhenius preexponential constant,
- $E$  activation energy,
- $R$  gas constant,
- $y = E/RT$ , and

$$p(y) = y^{-1} e^{-y} - \int_y^{\infty} y^{-1} e^{-y} dy.$$

For  $r$ =constant, Eq. (15) reduces to

$$\phi = k_1 p(y) \quad (16a)$$

and since  $\log p(y)$  is nearly linear with  $y$ , then

$$\log \phi \approx k_2 - 0.457E/RT. \quad (16b)$$

A method for deriving activation energy is based on the approximation that in the early stages of chemical reaction  $g(r)$  in Eq. (15) is nearly independent of  $r$ . It has been pointed out that the activation energy is then nearly independent of any assumption of zero-, first-, or second-order kinetics and that a first-order equation is a convenient one to use. Thus for

$$\frac{dr}{dt} = -kr,$$

we obtain

$$kt = - \int_1^r \frac{dr}{r} = g(r) - g(r_0) \approx \ln \left( \frac{1}{r} \right). \quad (17)$$

Eq. (15) becomes

$$\ln \ln \left( \frac{1}{r} \right) \approx \ln \frac{AE}{\phi R} + \ln p(y). \quad (18)$$

Using the same approximation for  $\log p(y)$  and putting  $\phi$ =constant, we get

$$\ln \ln \left( \frac{1}{r} \right) \approx k_3 - 0.457(\ln 10) \frac{E}{RT}. \quad (19)$$

The calculation of  $r$  from DTA thermograms for use in Eq. (19) is as follows. Since the numerical integration is carried out on the original instrument chart recordings, it is convenient to work in  $\int v dt$ . Eq. (14a) can be written

$$r = 1 - \left( v + \frac{B}{ms} \int_0^t v dt \right) \frac{s}{C\lambda}. \quad (14b)$$

For brevity, writing  $\int v dt = I$  (when  $r=0$ ,  $v=0$ ,  $I=I_{\max}$ ) and  $b=ms/B$ , we have

$$\frac{B}{ms} = \frac{C\lambda}{sI_{\max}} = \frac{1}{b}. \quad (20)$$

Eliminating unknowns from Eq. (14b) gives

$$r = 1 - \frac{vb+I}{I_{\max}}. \quad (21)$$

Finally, eliminating  $r$  from Eqs. (19) and (21)

$$\ln \ln \left( 1 - \frac{vb+I}{I_{\max}} \right)^{-1} \approx k_3 - \frac{0.457(\ln 10)E}{RT}. \quad (22)$$

Since  $\phi$  is known, the slope of the dotted line of Eq. (14a) yields the quantity  $b=ms/B$ . All quantities in the left-hand side of Eq. (22) are known. Activation energy can be obtained from a plot of the data using Eq. (22).

## 2.2 Present Method

We derived the equation for determination of the order of reaction, activation energy and frequency factor of decomposition reaction by DTA as follows.

The chemical reaction generally obeys

$$\frac{dx}{dt} = Ae^{-E/RT} (1-x)^n, \quad (23)$$

where  $x$ ,  $A$ ,  $E$ ,  $R$  and  $T$  are the same means as used above and  $n$  is the order of reaction. The rate of the reaction in the case where the temperature varies with time is given as follows

$$\frac{dx}{dt} = \left( \frac{\partial x}{\partial t} \right)_T + \left( \frac{\partial x}{\partial T} \right)_t \frac{dT}{dt}. \quad (2)$$

If the time coordinate is fixed, the number and position of the particles constituting the system are fixed and the rate of change of  $x$  with temperature,  $(\partial x / \partial T)_t$  should be zero. Hence, the total rate of reaction can be given by

$$\frac{dx}{dt} = Ae^{-E/RT} (1-x)^n. \quad (23)$$

The value of  $dx/dt$  increases to the maximum as the sample is heated in decomposition process. Differentiating both sides of Eq. (23) with respect to time, we get

$$\frac{d}{dt} \left( \frac{dx}{dt} \right) = -An(1-x)^{n-1} \frac{dx}{dt} e^{-E/RT} + A(1-x)^n e^{-E/RT} \frac{E}{RT^2} \frac{dT}{dt}. \quad (24a)$$

Using the heating rate of Eq. (9), Eq. (24a) becomes

$$\frac{d}{dt} \left( \frac{dx}{dt} \right) = \frac{dx}{dt} \left\{ \frac{E\phi}{RT^2} - An(1-x)^{n-1} e^{-E/RT} \right\}. \quad (24b)$$

When the rate of reaction is maximum,  $d/dt(dx/dt)$  is zero. Hence, at the temperature  $T_m$  where the maximum of  $dx/dt$  occurs, Eq. (24b) becomes

$$\frac{E\phi}{RT_m^2} = An(1-x)_m^{n-1} e^{-E/RT_m}, \quad (25)$$

where the subscript  $m$  means the value at the maximum of  $dx/dt$ . It is supported by Murray and White<sup>4)</sup> that the temperature  $T_m$  occurs when the deflection of the DTA curve is maximum.

Taking natural logarithms of both sides of Eq. (25), we get

$$\ln\left(\frac{E}{R}\right) + \ln\left(\frac{\phi}{T_m^2}\right) = \ln A + \ln n(1-x)_m^{n-1} - \frac{E}{RT_m}. \quad (26a)$$

Arranging Eq. (26a), the useful equation is obtained as follows

$$\ln \frac{\phi}{T_m^2 n(1-x)_m^{n-1}} = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m}. \quad (26b)$$

The fraction of remaining reactant at the temperature  $T_m$ ,  $(1-x)_m$  can be obtained from the treatment of the DTA curve with the Toop's method.

The left-hand side of Eq. (26b) is plotted against  $1/T_m$  with the value of  $n$  assumed. If the assumed value of  $n$  is correct, the straight line expressed by Eq. (26b) should be obtained. The slope of the straight line will be  $-E/R$  and the intercept will be  $\ln(AR/E)$ . Since  $R$  is known, the values of the activation energy and frequency factor are determined.

### 3 Experimental

#### 3.1 Materials

In the present study, magnesium hydroxide was used as a sample of rapid DTA measurements owing to low dehydration temperature. Magnesium hydroxide was purchased from Showa Chemical Co., Ltd. The photograph of the sample by Scanning Electron Microscope is shown in Fig. 1. Fig. 1 shows that the size of a particle of  $Mg(OH)_2$  crystal is about  $2 \times 3 \mu m$ . Magnesium hydroxide before used was dried in  $100 \sim 105^\circ C$  for 4 hr.

#### 3.2 Apparatus and Procedure

The present study was carried out by using Differential Thermal Analyzer of Mitamura Riken Kogyo Inc. This apparatus consists of the furnace with a vertical nickel sample holder and the associated controlling and recording equipments. The recording equipment consists of a amplifier and a recorder. The differential voltage in proportional to the temperature between the sample and the reference material is amplified by the DC stabilized amplifier, and the amplified differential voltage and the temperature of reference material are recorded on the same chart by the servo system. The sample and the reference material temperatures are measured in the center of the sample cup using platinum-platinum 13-percent-

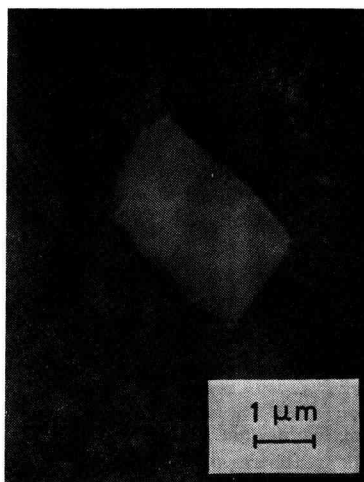


Fig. 1. Photograph of magnesium hydroxide used in this work by Scanning Electron Microscope ( $\sim \times 10^4$ ).

rhodium thermocouples. The furnace temperature is controlled by a automatic voltage modulator. Any heating rate up to about  $25^\circ\text{C}/\text{min}$  can be selected in this equipment. Sample cups are quartz tubes being 4 mm in inner diameter and 11.5 mm in length.

The reference material in this work was  $\alpha$ -aluminium oxide and the quantity used approximately 0.150 g. Approximately 0.020 g of magnesium hydroxide was used in each DTA run. Loading of magnesium hydroxide into the sample cup was fixed. The sample was loosely loaded into the cup only by rolling it with no tapping. The DTA runs were carried out changing the heating rate without evacuating system.

#### 4 Results and Discussions

The dehydration of magnesium hydroxide is as follows:



Since the weight loss after run in the DTA was in agreement with the weight of  $\text{H}_2\text{O}$  contained in the sample, this reaction was verified.

The typical DTA curve of the above reaction obtained in this study is shown in Fig. 2. The DTA curves were treated with the two previous methods, that is, the Kissinger's method and the Toop's method, and with the present method for determining the kinetic constants of the above reaction.

The value of integral  $I = \int v dt$  in Eq. (22) was obtained by weighing the area of peak corresponding to the integral  $I$  on the recording paper.

In Fig. 2, it is observed that the base line deflects after the completion of reaction. The deflection of the base line is caused by the difference of heat capacities of  $\text{Mg}(\text{OH})_2$  and  $\text{MgO}$ , when the heating rate is large. In this curve, to obtain the value of  $I$ , the analytical method proposed by Adam and Müller<sup>6)</sup> was used for the treatment of peak area. This analytical

method is illustrated in Fig. 2.

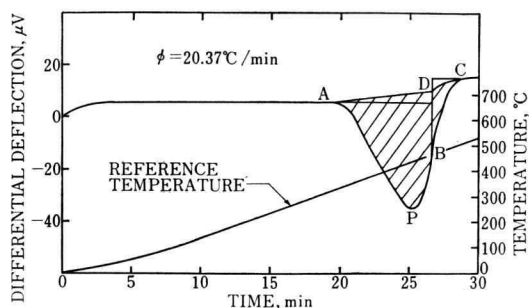


Fig. 2. Typical DTA curve of magnesium hydroxide.

The endothermic peak in the region 330 to 500°C results from the dehydration of magnesium hydroxide. The peak temperature varies with heating rate.

In Fig. 2, a straight line is drawn from the starting point of reaction A to the point D in the half of the distance between the base line before the reaction and that after the reaction. Moreover, the point D is equal to the final point of reaction B with time coordinate. The exponential curve from D to C has the same dumping factor as that from B to C has. The area of peak is shaded in Fig. 2. The area of peak in the DTA curve is proportional to quantity of heat of reaction, and Adam et al.<sup>6)</sup> consider that the shaded area in Fig. 2 approximately corresponds to quantity of heat of reaction when the base line deflects after completion of reaction.

The values of  $n$ ,  $E$  and  $A$  obtained by the present and the two previous methods are shown in Table 1. The values reported by other workers<sup>7-9)</sup> are shown in Table 2 for comparison.

The values of  $n$ ,  $E$  and  $A$  can be determined concurrently only by the present method as shown in Table 1. It is assumed in the two previous methods that the decomposition reaction obeys the first-order law.

The plots for the determination of activation energy by the Kissinger's and the Toop's methods and of  $n$ ,  $E$  and  $A$  by the present method are shown in Fig. 3, Fig. 4 and Fig. 5, respectively.

Table 1. Values of order of reaction  $n$ , activation energy  $E$  and frequency factor  $A$  for dehydration of magnesium hydroxide determined in this work.

Source	$n$	$E$ (kcal/mol)	$\ln A$
Present method	0.8	63.20	46.47
Kissingers' method	1 <sup>a</sup>	62.49	45.98
Toop's method	1 <sup>a</sup>	58.88	

<sup>a</sup> Assumed value

Table 2. Reported values of order of reaction  $n$  and activation energy  $E$  for dehydration of magnesium hydroxide by means of isothermal weight loss measurements in vacuum.

Source	$n$	$E$ (kcal/mol)
Gregg and Razouk <sup>a</sup>	0.67	12-27 <sup>d</sup>
Anderson and Horlock <sup>b</sup>	0.5	23.6 <sup>e</sup> , 27.6 <sup>d</sup>
Gordon and Kingery <sup>c</sup>	0.5-1	29-32 <sup>e</sup>

<sup>a</sup> Ref. (7)    <sup>b</sup> Ref. (8)    <sup>c</sup> Ref. (9)

<sup>d</sup> Prepared samples    <sup>e</sup> Single crystals

If the dehydration of magnesium hydroxide obeys the first-order law, the straight line should be obtained in the plots of Fig. 3 and Fig. 4. Hence, from Fig. 3 and Fig. 4, it is predicted that the dehydration of magnesium hydroxide do not obey the first-order law.

In the present method, the straight line was obtained by trial-and-error attempts to determine the order of reaction. When the value of  $n$  was set to be 0.8, the straight line was obtained. The value of  $E$  determined by the present method agrees well with those by the two previous methods. Moreover, the value of  $n$  of the present method is in the range of the values reported by other workers<sup>7-9</sup>) as shown in Table 1 and Table 2. From these results, the present method may be confirmed. The present method is valid for reaction characterized by order of reaction, activation energy and frequency factor, except labor of trial-and-error attempts to obtain the straight line.

The values of  $E$  determined in this work for dehydration of magnesium hydroxide are much higher than those reported by other workers<sup>7-9</sup>). It is supposed that this result is due

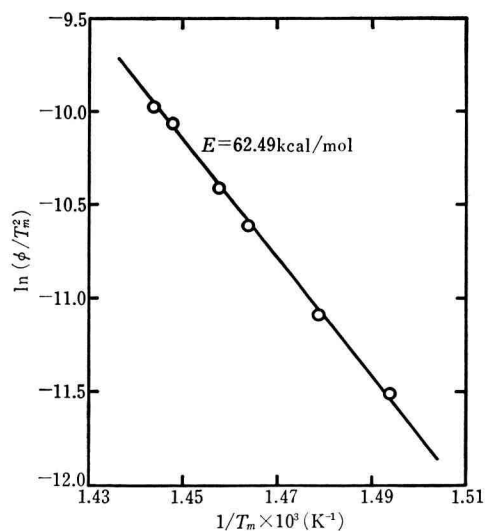


Fig. 3 Plot of  $\ln(\phi/T_m^2)$  against  $1/T_m$  of Eq. (6) to determine activation energy by the Kissinger's method.

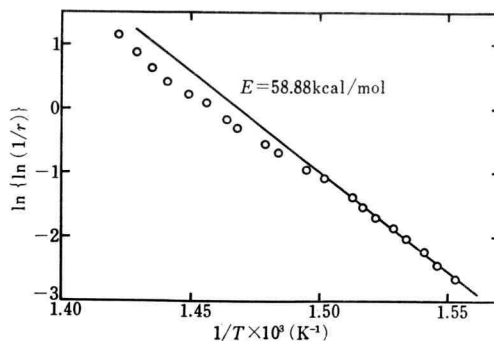


Fig. 4. Plot of  $\ln\{\ln(1/r)\}$  against  $1/T$  of Eq. (22) to determine activation energy by the Toop's method.

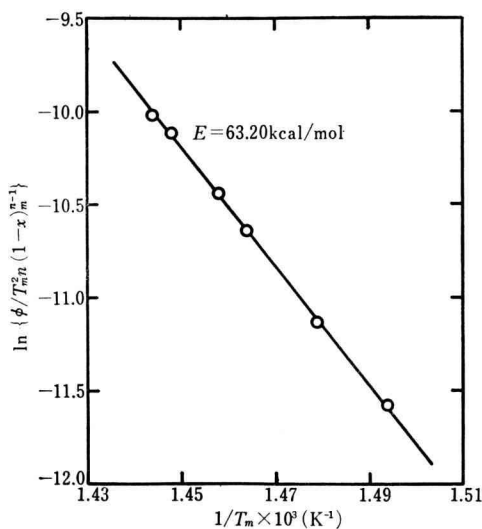


Fig. 5. Plot of  $\ln\{\phi/T_m^2 n (1-x)_m^{n-1}\}$  against  $1/T_m$  of Eq. (26b) to determine the values of  $n$ ,  $E$  and  $A$  concurrently by the present method.

to the difference on preparation of magnesium hydroxide, and this result do not disturb the validity of the present method.

Variation of fraction of reactant decomposed at peak temperature with heating rate is argued taking the example of dehydration of magnesium hydroxide below. Fraction of reactant decomposed at peak temperature,  $(1-r)_m$  is defined from Eq. (26b) as follows

$$\ln(1-r)_m = 1 - \frac{1}{n-1} \left( \ln \frac{\phi E}{T_m^2 A R} + \frac{E}{R T_m} \right) + \ln n. \quad (27)$$

It is seen from Eq. (27) that since  $n$ ,  $E$  and  $A$  are constants  $(1-r)_m$  is function of  $\phi$  and  $T_m$ . And  $T_m$  becomes higher with increase of  $\phi$  as also verified in this work. (See Table 3.)

It was found from Table 3 that the decreases heating rate results in the large fraction of the

reactant decomposed at peak temperature, where the heating rate is below about 15°C/min. But, this tendency disappears for the heating rate above 20°C/min. The further experiment will have to be carried out to confirm this tendency.

Table 3. Variations of peak temperature with heating rate and of fraction of reactant decomposed at peak temperature.

Heating rate $\phi$ (°C/min)	Peak temperature $T_m$ (K)	Fraction of reactant decomposed at peak temperature $(1-r)_m$
4.55	669.51	0.769
7.06	675.93	0.741
11.62	682.89	0.727
14.24	685.95	0.718
20.37	690.59	0.749
22.50	692.71	0.735

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