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DETERMINATION OF THE KINETIC PARAMETERS FROM DIFFERENTIAL THERMAL ANALYSIS

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A theory of differential thermal analysis for a block-type system with spherical cells packed with inert material is developed. From the solution of DTA equations, a method for determining the reaction order, activation energy and frequency factor of the Arrhenius equation is presented. This method is applied to the decomposition of magnesite. The agreement between theory and experiment is very good.

A number of investigators studied the reaction kinetics utilizing differential thermal analysis and there are several schemes used for the determination of the kinetic parameters from DTA curves. The method presented by Borchardt and Daniels [1] for a stirred solution system was successful, although somewhat tedious. This method was expanded and modified by Freeman and Carroll [2], Reed, et al. [3] and more recently by Reich [4] and Fatu [5]. This method was also used with some degree of success by these people for the system other than the stirred solution system. However, the required experimental condition that there is no temperature gradient in the sample or reference cell was not obtained for the usual DTA system. The method of Kissinger [6] appears to be useful, but lacks theoretical justification.

In the present paper, a theory of block-type DTA with spherical cells is developed. Based on the results obtained, a method for the determination of reaction order, activation energy, and frequency factor of the Arrhenius equation is presented. The method is then applied to the decomposition reaction of magnesite. The spherical cell is chosen mainly because it is easy to approximate experimentally. This is the first known attempt to determine the kinetic parameters using the DTA theory where there is a temperature gradient in the cell.

Theory

A precise theory was developed by Akita and Kase [7] for a block-type DTA with cells that are infinite cylinders. Since the following derivation of theory parallels that of Akita and Kase, their nomenclature is followed here.

Consider two spherical cells which are packed with inert material and a small amount of reactant is mixed in one, the sample cell. If the thermal constants of the cell are virtually insensitive to temperature, the differential equations for reference and sample cells are given by

$$\frac{\partial T_1}{\partial t} = K_1 \left(\frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right) \tag{1}$$

$$\frac{\partial T_2}{\partial t} = K_2 \left(\frac{\partial^2 T_2}{\partial r^2} + \frac{2}{r} \frac{\partial T_2}{\partial r} \right) + \frac{Q W_0}{C_2 W_2} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{W}{W_0} \right) \tag{2}$$

with initial and boundary conditions

$$T = T_0 \qquad \text{at} \quad t = 0 \tag{3}$$

$$T = T_0 + \phi t \quad \text{at} \quad r = a \tag{4}$$

Here T is the temperature, r is the radial coordinate, K is the thermal diffusivity of packed material, Q is the heat of reaction per weight, C is the specific heat, W_0 is the original weight of reactant, W_2 is the total weight of sample cell, W is the weight of reacted reactant, t is the time, ϕ is the heating rate, and a is the radius of the cell. The subscripts 1 and 2 refer to the reference and sample cell, respectively. The initial temperature, T_0, is usually regarded as the temperature at which the DTA curve departs from the base line.

We assume that the reaction rate is given by the Arrhenius equation

$$k = Z \exp \left(- \frac{E}{R T_2} \right) \tag{5}$$

where k is the reaction rate, Z is the frequency factor, E is the activation energy, and R is the gas constant. The reaction rate term of Eq. (2) becomes

$$\frac{Q W_0}{C_2 W_2} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{W}{W_0} \right) = \frac{Q W_0}{C_2 W_2} \left(1 - \frac{W}{W_0} \right)^{\mathrm{n}} k \tag{6}$$

where n is the order of reaction.

The temperature change in the sample cell as a result of the reaction is very small with respect to the heating temperature and the temperature rise on the cell surface up to peak temperature is much smaller than T_0. Thus we have

$$T_2(T_0 - \phi t) \simeq (T_0 + \phi t)(T_0 - \phi t) \simeq T_0^2 \tag{7}$$

We now integrate Eq. (6) from $t = 0$ to $t = t$ after substituting Eq. (7) into Eq. (5) and the resulting equation into Eq. (6). Then we have, after some algebraic manipulation,

$$\frac{Q W_0}{C_2 W_2} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{W}{W_0} \right) = \delta_{\mathrm{n}} \exp (\alpha t) \left[1 - \frac{1}{X} \exp (\alpha t) \right]^{\mathrm{n}/(1-\mathrm{n})} \tag{8}$$

where

$$X \equiv \frac{1}{1 - n} \frac{\alpha}{A} + 1 \tag{9}$$

$$\delta_n \equiv \frac{QW_0}{C_2W_2} A \left[1 + \frac{A}{\alpha}(1 - n)\right]^{n/(1-n)} \tag{10}$$

$$\alpha = E\phi/RT_0^2 \tag{11}$$

$$A = Z \exp\left(-\frac{E}{RT_0}\right) \tag{12}$$

For the case where $n = 1$, we have

$$\frac{QW_0}{C_2W_2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{W}{W_0}\right) = \delta_1 \exp(\alpha t) \exp\left[-\frac{A}{\alpha}\exp(\alpha t)\right] \tag{13}$$

where

$$\delta_1 \equiv \frac{QW_0}{C_2W_2} A \exp\left(\frac{A}{\alpha}\right) \tag{14}$$

Now we make the following transformation

$$\Theta_2 = T_2 - T_0 + \delta_n \frac{X}{\alpha}(1 - n)\left[\left[1 - \frac{1}{X}\exp(\alpha t)\right]^{1/(1-n)} - \left(1 - \frac{1}{X}\right)^{1/(1-n)}\right] \tag{15}$$

and in the case when $n = 1$

$$\Theta_2 = T_2 + T_0 - \frac{\delta_1}{A}\exp\left[-\frac{A}{\alpha}\exp(\alpha t)\right] + \frac{\delta_1}{A}\exp\left(-\frac{A}{\alpha}\right) \tag{16}$$

We introduce the new variable

$$P_n(l) \equiv \delta_n \frac{X}{\alpha}(1 - n)\frac{(-1)^l}{l!}\,\frac{\Gamma\left(\dfrac{2-n}{1-n}\right)}{\Gamma\left(\dfrac{2-n}{1-n} - l\right)}\,\frac{1}{X^l} \tag{17}$$

and again when $n = 1$,

$$P_1(l) \equiv \frac{\delta_1}{A}\frac{(-1)^l}{l!}\left(\frac{A}{\alpha}\right) \tag{18}$$

By introducing the assumption that $|\exp(\alpha t)/x| < 1$ for the nth order reaction, Eqs (2), (3), and (4) become

$$\frac{\partial \Theta_2}{\partial t} = K_2\left(\frac{\partial^2 \Theta_2}{\partial r^2} + \frac{2}{r}\frac{\partial \Theta_2}{\partial r}\right) \tag{19}$$

$$\Theta = 0 \quad \text{at} \quad t = 0 \tag{20}$$

$$\Theta = \phi t + \sum_{l=n}^{\infty} P_n(l)\left[\exp(l\alpha t) - 1\right] \quad \text{at} \quad r = a \tag{21}$$

It should be remembered that Eq. (21) for first order will have $P_1(l)$ in place of $P_n(l)$ and all changes should be made accordingly.

As the transformed DTA equations are identical for first and nth order reactions, for simplicity we shall solve the equation for first order reaction. The problem now reduces to that of the heat conduction in a sphere with zero initial temperature and changing surface temperature with time. The solution is [8]

$$\Theta_2 = \frac{2}{ar}\sum_{m=1}^{\infty} \exp\left(-\frac{K_2 m^2 \pi^2 t}{a^2}\right) \sin\left(\frac{m\pi r}{a}\right)(-m\pi K_2)(-1)^m \int_0^t \exp\left(\frac{K_2 m^2 \pi^2 \lambda}{a^2}\right) \xi(\lambda)\,\mathrm{d}\lambda \tag{22}$$

with

$$\xi(\lambda) = \phi\lambda + \sum_{l=0}^{\infty} P_1(l)\left[\exp(l\alpha\lambda) - 1\right] \tag{23}$$

The integration is very tedious but straightforward. The solution for the reference cell can be found by setting $P_1(l) = 0$ and the DTA curve is the temperature difference between the sample and reference cells. Furthermore, the temperature at the center of the cells can be found by taking the limit of the solution as r approaches zero.

Now we assume that K_1 is the same as K_2. This should be reasonable when a small amount of reactant is mixed with inert materials in the cell. We further assume the following, which is also reasonable for most experimental conditions; i.e., when reasonable values are substituted, the second term in the parenthesis is much smaller than unity.

$$\left(1 + \frac{l\alpha a^2}{K_2 m^2 \pi^2}\right)^{-1} \simeq \left(1 - \frac{l\alpha a^2}{K_2 m^2 \pi^2}\right) \tag{24}$$

Finally we obtain

$$\Delta T = \left(\frac{r^2 - a^2}{6K_2}\right) \sum_{l=0}^{\infty} P_1(l) \exp(l\alpha t) \cdot l\alpha - \frac{2a^3}{K_2 \pi^3 r} \sum_{m=1}^{\infty} \exp\left(-\frac{K_2 m^2 \pi^2 t}{a^2}\right) \sin\left(\frac{m\pi r}{a}\right) \frac{(-1)^m}{m^3} \sum_{l=0}^{\infty} P_1(l) \cdot l\alpha \tag{25}$$

However, the second term in Eq. (25) is numerically insignificant compared with the first term except when it is near zero. Therefore, we can safely ignore the second term

$$\Delta T_c \cong \frac{-a^2}{6K_2} \sum_{l=0}^{\infty} P_1(l) l\alpha \cdot \exp(l\alpha t) = \frac{-a^2}{6K_2} \frac{QW_0}{C_2 W_2} \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{W}{W_0}\right) \tag{26}$$

For nth order reaction, Eq. (8) should be combined into Eq. (26).

The DTA curve can be generated numerically by Eq. (26) and accordingly the effect of variables on the DTA curve can be easily investigated. The behavior of the curve to the changes in heating rate, order of reaction, activation energy, and frequency factor followed the same trends as reported in the literature [3, 7].

Determination of kinetic parameters

Since the DTA curve is obtained in Eq. (26), we can relate this equation to experimental quantities to determine the kinetic parameters. We shall study the first order and *n*th order reactions, separately.

First order reaction

At the maximum of DTA curve, we have the relationships

$$\alpha t_m = \ln\left(\frac{\alpha}{A}\right) \tag{27}$$

where subscript *m* refers to the maximum. Then the height of the curve is

$$\Delta T_m = \frac{a^2}{6K_2}\frac{QW_0}{C_2W_2}\left(\frac{1}{e}\right)\alpha\cdot\exp\left(\frac{A}{\alpha}\right) \tag{28}$$

At time of $t_{1/2m} = \frac{1}{2}t_m$ we have

$$\Delta T_{1/2m} = \frac{a^2}{6K_2}\frac{QW_0}{C_2W_2}(A\cdot\alpha)^{1/2}\exp\left(\frac{A}{\alpha}\right)^{1/2} \tag{29}$$

Thus, we have

$$A = \frac{(\Delta T_{1/2m})^2}{\Delta T_m}\left(\frac{1}{e}\right)\left(\frac{6K_2}{a^2}\frac{C_2W_2}{QW_0}\right) \tag{30}$$

Once A is known, E and Z can be easily obtained from Eqs (27) and (12).

However, since the thermal properties of the cell and packing in the last bracket of Eq. (30) are not usually known, we may need two experiments with different heating rates. Then, from Eq. (27) we obtain the following relationship:

$$E = \frac{RT_0^2}{(\phi t_m)_I - (\phi t_m)_{II}}\ln\frac{(\phi)_I}{(\phi)_{II}} \tag{31}$$

where the subscripts outside the parenthesis refer to the different experimental runs.

nth order reaction

At the maximum of DTA curve, we obtain

$$\alpha t_m = \ln\left[\frac{\alpha}{A} + (1-n)\right] \tag{32}$$

and from this we get

$$\Delta T_m = \frac{a^2}{6K_2}\,\frac{QW_0}{C_2W_2}\,\alpha\left[\frac{An^n}{\alpha}\exp(\alpha t)\right]^{1/(1-n)} \tag{33}$$

From Eqs (8) and (26) we obtain the following condition for the end of the DTA curve:

$$X = \exp(\alpha t_f) \tag{34}$$

where t_f is the time of the completion of DTA curve. This leads to the relationship

$$n = 1 - \exp[\alpha(t_m - t_f)] \tag{35}$$

If we take any time, t_a, and the corresponding differential temperature, ΔT_a, then, from Eqs (26), (32) and (33) we have

$$\frac{n}{1-n}\ln\left(\frac{e^{\alpha t_f} - e^{\alpha t_m}}{e^{\alpha t_f} - e^{\alpha t_a}}\right) = \ln\left(\frac{\Delta T_m}{\Delta T_a}\,\frac{e^{\alpha t_a}}{e^{\alpha t_m}}\right) \tag{36}$$

Thus, we have two unknowns, n and E, and two equations (35) and (36). Once these values are determined the value of Z can be readily calculated. Note here that only a single DTA curve is required in this case.

Experimental

To verify the methods for the determination of kinetic parameters, the decomposition reaction of magnesite was studied.

Since it is difficult to build spherical cells, we used cylindrical cells of equal height and diameter. The discrepancy between theory and this experimental setup would be small, especially at the center of the cell where the chromel-alumel thermocouples are placed. Two cylindrical cells of 0.95 cm diameter were drilled in the metal body and close fitting plugs were used to make the cell of desired shape. The cells were filled with Norton Alundum whose weight was 1155 mg in each cell. The cells were not rigidly sealed so that there is no pressure in the cell.

The magnesite* was used as a sample. An amount of 228 mg was mixed with Alundum in the sample cell and the whole DTA block was placed inside a furnace.

Results and discussion

Three different heating rates were employed in the experiment. The results are summarized in Table 1 where the heating rate, time, and corresponding differential temperature are given.

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* Obtained from Fischer Scientific Co.

The DTA peak started at 350° which was taken to be T_0. Using Eqs (35) and (36) the reaction order and activation energy were found for each run. By Eqs (12) and (32) the value of the frequency factor was also calculated. These values are listed in Table 2. The result of Run II gives values somewhat different from those of other runs. This may be due to experimental uncertainties such as the uneven mixing of sample with inert material in the cell. This kind of small variation is expected.

Table 1

Experimental results

Run	Φ, °C/min	t_m, min	t_a, min	t_f, min	ΔT_m, μV	ΔT_a, μV
I	1.75	34.3	22.9	47.0	12.9	5.2
II	3.49	20.2	13.5	26.8	32.0	12.0
III	5.56	14.0	9.3	18.2	44.7	12.1

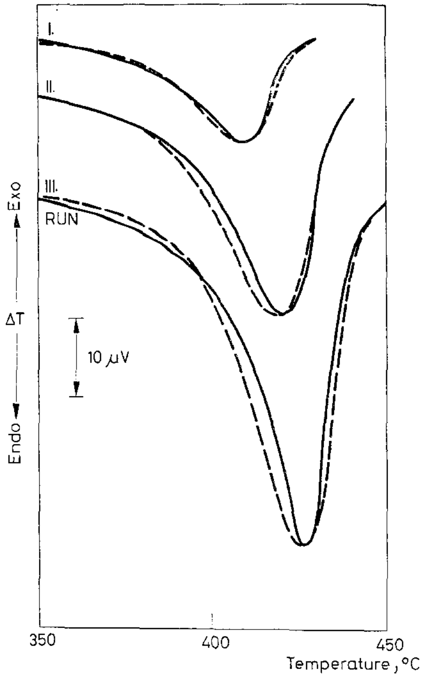

Fig. 1. Comparison between theory and experiment on the decomposition of magnesite; —— experimental, - - - calculated

Table 2

Kinetic parameters obtained

Run	n	E, kcal/mole	log Z
I	0.83	61.5	18.7
II	0.81	56.0	16.9
III	0.84	60.6	18.3

With the values in Table 2 the DTA curves were generated and compared with experiment in Fig. 1. Since the value of

$$\frac{a^2}{6K_2}\,\frac{QW_0}{C_2W_2}$$

is not known and this value affects only the magnitude or height of the DTA curve, the calculated curve was forced to fit the experiment at the maximum peak height. The agreement between theory and experiment is very good in spite of those assumptions involved in the derivation of the theory.

A review of the literature on the decomposition of magnesite shows conflicting results on the decomposition temperature. It is listed to be 350° in several places [9, 10]. This temperature corresponds well with our observed value. However, it is also reported that magnesite decomposes at about 550° with an activation energy of about 36 kcal/mole and a reaction order of unity in one case [11] and about 0.58 on other occasions [6, 12]. Unfortunately, there are no data on the decomposition at 350°. The present data on reaction rate and activation energy are significantly different from those reported.

Conclusion

The agreement between theory and experiment shows that the assumptions made in the derivation of theory are reasonable. Furthermore, the spherical cell in the theory may be approximated experimentally by a cylindrical cell of equal height and diameter. The method presented here for the determination of kinetic parameters from the DTA curve is a consequence of the theory and is reliable as shown in the example of magnesite decomposition.

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Résumé — On développe une théorie de l'analyse thermique différentielle pour un système de type "bloc" avec cellules sphériques remplies d'une substance inerte. On présente une méthode pour déterminer l'ordre de la réaction, l'énergie d'activation et le facteur de fréquence de l'équation d'Arrhenius à partir de la solution des équations trouvées pour l'ATD. La méthode est appliquée à la décomposition de la magnésite. L'accord entre la théorie et l'expérience est très bon.

Zusammenfassung — Eine Theorie der Differentialthermoanalyse für ein Blocksystem von mit Inertstoff gefüllten sphärischen Zellen wurde entwickelt. Die Gleichungen ermöglichen die Bestimmung von Reaktionsordnung, Aktivierungsenergie und Frequenzfaktor der Arrheniusschen Gleichung. Die Methode wurde bei der Zersetzung von Magnesit angewandt und gute Übereinstimmung zwischen den theoretischen Erwägungen und den praktischen Resultaten erzielt.

Резюме — Разработана теория дифференциального термического анализа для системы блокового типа с шариковыми ячейками, наполненными инертным веществом. На основании решения уравнений ДТА дан метод определения порядка реакции, энергии активации и фактора частоты уравнения Аррениуса. Метод использован при исследовании распада магнезита. Наблюдается очень хорошее совпадение между теорией и экспериментом.