Journal of Thermal Analysis, Vol. 50 (1997) 269-277

Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

EVALUATION OF KINETIC PARAMETERS FROM A SINGLE TG CURVE BASED ON THE SIMILARITY THEORY AND PROCESS SYMMETRY

I. L. Lapides

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem,
91904 Jerusalem, Israel

Abstract

The equation for calculation of the activation energy of the diffusion of the evolved products through the matrix (E) from a single TG curve were proposed by solving Fick's laws. The solution is based on the similarly theory by utilizing a Fourier number.

The proposed method was examined by using mass loss data for the dehydroxylation of some micas with and without FeO (muscovite and its varieties and lepidolite) as determined from their TG curves. The E values for the first stage of the dehydroxylation of these micas are E_1=85±10 kJ mol^{-1}; for the final stage E_2=380±40 kJ mol^{-1} and for the mass loss connected with fluorine E_F=85±10 kJ mol^{-1}.

Keywords: activation energy, dehydroxylation, diffusion, integral criterion of Fourier, mica, similarity theory, TG curve

Introduction

The kinetics of the thermal solid state transformations has been described by different equations [1]. For isothermal experiments, a general equation may be obtained by simplification of the model reactions:

$$K = \mathrm{d}\alpha/\mathrm{d}\tau = k_o f(\alpha); \tag{1}$$

$$k_o = A_o \exp(-E/RT) \text{ – Arrhenius equation;} \tag{2}$$

$$f(\alpha) = \alpha^{a}(1-a)^{\beta};\ f(\alpha) = (1-a)^{n} \text{ or } f(\alpha) = \alpha^{n}; \tag{3}$$

$$K = A_o \exp(-E/RT) f(\alpha); \tag{4}$$

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

where K is the rate of reaction, α – the decomposed fraction of substances, τ – the reaction time, k_0 – the reaction rate constant, E – the activation energy, T – the temperature in K, R – the gas constant, n – the order of reaction.

In the literature one can find an enormous number of publications on non-isothermal kinetics [2–7]. Under non-isothermal experimental conditions, with a constant heating rate of the sample, kinetic equations become:

$$\mathrm{d}\alpha/\mathrm{d}T=(A_0/b)\exp(-E/RT)f(\alpha); \tag{5}$$

$$\frac{\mathrm{d}\alpha}{f(\alpha)}=(A_0/b)\exp(-E/RT)\mathrm{d}T; \tag{6}$$

$$F(x)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)};\ \frac{AE}{bR}\int_x^{\infty}\frac{\mathrm{e}^{-x}}{x^2}\mathrm{d}x=\frac{AE}{bR}P(x); \tag{7}$$

where $b=\mathrm{d}T/\mathrm{d}\tau$ – is the heating rate, $F(x)$ – the weight integral, $P(x)$ – the temperature integral.

There are many publications where different $F(x)$ and $P(x)$ approximations are used for different reaction mechanisms [2]. In general solid-state thermal reactions are complicated and multi-staged [8–13],but the activation energy values determine quantitatively the changes in amounts of the reaction products obtained with time. The activation energies of the different stages of the non-isothermal dehydroxylation of micas were calculated according to the present method and compared with values calculated by means of two other widely accepted methods [6, 7].

Only two methods were used in this work for calculation of the activation energy of the thermal dehydration or dehydroxylation of micas for comparison with the proposed method.

Horowitz and Metzger [6] used the equation $F(\alpha)=\alpha^n$. After some simplifications of Eqs (5–7) they determined n from the TG and DTG curves and later E from the parameters of the straight line in the coordinates:

$$\ln\ln C \quad vs. \quad \Theta\ (n=1) \tag{8}$$

or

$$\begin{gathered}\ln(1-C^{1-n}) \quad vs. \quad \Theta\ (n\neq 1)\\ C=(W_t-W_f)/(W_o-W_f)\end{gathered} \tag{9}$$

where W_t – is the mass of sample at temperature T, W_0 – the mass of sample at the initial temperature T_0 of the thermal effect, W_f – the mass of sample after the termination of the reaction, $T=T_s+\Theta$, T_s – the temperature of the DTG peak.

Coats and Redfern [7] used the expression $d\alpha/d\tau=K(1-\alpha)^n$ together with an expansion of the exponential function (6) into a series. Solution of these equations permits graphical evaluation of E in the coordinates

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] \quad vs. \quad \frac{1}{T}(n=1) \tag{10}$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad vs. \quad \frac{1}{T}(n\neq 1) \tag{11}$$

It should be noted that for n=1/2; 1/3; 2/3 or 1, similar E values are obtained from (10) and (11). Equations (10) and (11) are valid for E>40 kJ mol^{-1}.

Diffusion model

If we consider a case in which the transformation rate is determined by the transport of single atoms, molecules or radicals through the solid phase, the common reaction rate is the rate of the diffusion process. In this case all of the solutions are based on the mass transfer equations (Fick's laws equations I and II):

$$\text{(I)} \qquad I_A=-D\frac{\partial C_A}{\partial x}; \tag{12}$$

$$\text{(II)} \qquad \frac{\partial C_A}{\partial x}=\frac{\partial}{\partial x}(-I)=-\frac{\partial^2 C_A}{\partial x^2}; \tag{13}$$

The boundary conditions and the symmetry of the diffusion process, or the reacting bodies, must also be taken into account. These boundary conditions are the concentrations of the diffusion phase as a function of the coordinates (x) and time (τ):

$$-D\frac{\partial C_A}{\partial x}=\beta(C_{Ai}-C_A); \quad C_A(x,\tau) \tag{14}$$

where C_{Ai} is the equilibrium concentration at the phase boundaries A_i.

In the present paper the methods of the similarity theory were used [14] to solve the common equations of diffusion (12 and 13).

This theory utilizes some numbers (criteria) of similarity as the diffusion number of Fourier Fo, the diffusion number of Bio, etc.

$$Fo=\frac{D\tau}{a^2}; \tag{15}$$

where a – is the effective radius of a solid particle, D – the diffusion coefficient.

An equation which is analogous to the Arrhenius Eq. (2) can be applied to describe D as follows:

$$D=D_0\exp(-E/RT) \tag{16}$$

where D_0 is the pre-exponential factor.
The Fourier number Fo characterizes an alteration of the diffusion mass transfer in our case when $T=T(\tau)$.

In this stage the solution corresponds to the structure symmetry of the reacting bodies or the symmetry of the diffusion directions. Since the data used in the present communication were those of the thermal decomposition of micas which are layer silicates [9, 10], we applied a model for diffusion from an infinite plate. The solution in this case is as follows [14]:

$$\frac{Q}{Q_0}=1-2\sqrt{\frac{Fo}{\pi}}+\left[4\sqrt{Fo}\sum_{n-1}^{\infty}(-1)^{n-1}\,\mathrm{ierfc}\,\frac{n}{\sqrt{Fo}}\right] \tag{17}$$

where Q_0 and Q are amounts of diffusion components, initially and at time τ, respectively.
The value of the expression in brackets is $<10^{-3}\,Fo$ and can be neglected. Equation (17) simplifies to

$$\frac{Q}{Q_0}=1-\mathrm{Const}\sqrt{Fo}\quad\text{or}\quad\alpha=\mathrm{Const}\sqrt{Fo} \tag{18}$$

The integral Fourier criterion may be used for the next solution [15]. When the heating rate is a linear function of the temperature, Fo is

$$Fo=\frac{1}{a^2}\int_{\tau_0}^{\tau}D(\tau)\mathrm{d}\tau=\frac{D_0}{a^2}\int_{\tau_0}^{\tau}\exp(-E/Rb\tau)\mathrm{d}\tau=\frac{D_0}{ba^2}\int_{T_0}^{T}\exp(-E/RT)\mathrm{d}T; \tag{19}$$

where τ_0, T_0 are the time and temperature at the start of the reaction. Since $E \gg RT$, it is possible, according to [16], to change one of the limits of the integral (19) from T_0 to 0:

$$Fo=\frac{D_0}{ba^2}\int_{0}^{T}\exp(-E/RT)\mathrm{d}T; \tag{20}$$

The solution of a similar integral can be found in the literature [17] and is connected with the function:

$$E_i(-x) = \int_{-\infty}^{-x} \frac{e^x}{x}\,dx$$

The solution for *Fo* is:

$$Fo = \frac{D_o E}{a^2 bR}\left[\frac{RT}{E}\exp(-E/RT) + E_i(-E/RT)\right] \tag{21}$$

In our case $E>>RT$, i.e. $x>>1$ and

$$E_i(-x) \cong e^x \frac{1-x}{x^2} \qquad [17].$$

Thus,

$$Fo = \frac{D_o}{ba^2} R \frac{T^2}{E} \exp(-E/RT) \tag{22}$$

It is possible to find the *E* value by solving the transcendental equation on the basis of (21):

$$\frac{Fo_1}{Fo_2} = \eta = \frac{T_1 \exp(-E/RT_1) + \frac{E}{R} E_i(-E/RT_1)}{T_2 \exp(-E/RT_2) + \frac{E}{R} E_i(-E/RT_2)} \tag{23}$$

or, approximately, on the basis of (22):

$$E = \frac{R(\ln\eta - 2\ln T_1/T_2)}{1/T_2 - 1/T_1} \tag{24}$$

The value $\eta = Fo_1/Fo_2$ may be calculated from (18) or, using Fo_1 and Fo_2 from the plot for *Fo* which must take into account the process symmetry [14]. In the mica case we can apply the curve of the plate model mentioned above (Fig. 1 from [14]) for the determination of *Fo* in accordance with the value $\alpha=\alpha(T)$. Only two points of the function $\alpha=\alpha(T)$ were used for calculation of *E* from (23) and (24). The accuracy of the *E* value may be increased by plotting several points. For this purpose one must transform (22) to

$$\ln(Fo/T^2) = A - E/RT \tag{25}$$

where

$$A = \frac{D_o R}{a^2 bE};$$

Thus, a plot may be constructed with the coordinates

$$\ln(Fo/T^2) \quad vs. \quad 1/T \tag{26}$$

A straight line is evidence for the validity of the diffusion hypothesis. The E value in this case was determined from the slope and the A value from the intercept of the straight line.

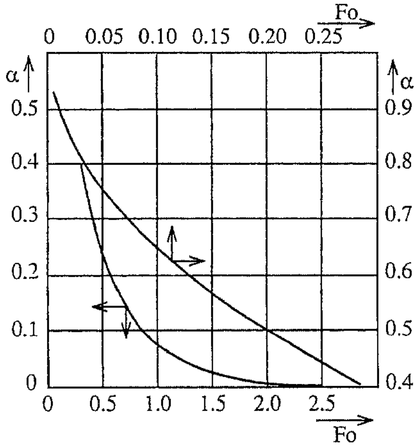

Fig. 1 Values of Fo vs. α for an infinite plate model (from [14])

Testing of the models

Experimental data (mass *vs.* temperature) of different micas, especially of muscovite $\{KAl_2(AlSi_3)O_{10}(OH)_2\}$ and its varieties, and lepidolites $\{K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2\}$ were taken from TG and DTG curves published in our earlier papers [9, 10].

Figure 2 shows curves determined from calculations according to the models of Horowitz-Metzger (9), Coats-Redfern (11) for six different samples. Figure 3 shows curves obtained from calculations by the present model for the same six samples.

Mass loss in the TG and DTG curves of these micas is due to dehydroxylation, and in micas which contain fluorine, also, due to their defluorination. In the TG and DTG curves of one sample, phengite-muscovite with Σ(FeO, MnO, MgO and CaO)$\approx$4%, the oxidation of Fe^{2+} and Mn^{2+} affects the shape of the curves and the mass loss.

By comparing Figs 2 and 3 it may be observed that most points which were calculated according to the diffusion model, fall on straight lines, whereas only part of the points which were calculated according to the models of Horowitz-

Metzger (9) and Coats-Redfern (11) fall on straight lines. Thus, for this thermal dehydroxylation process of micas the diffusion model seems to be preferable.

The average E value for all samples (except phengite-muscovite) is: for the first stage of the dehydroxylation, E_1~85±10 kJ mol^{-1}, and for the second stage, E_2~380±40 kJ mol^{-1}. For the phengite-muscovite, where the TG curve includes the oxidation process of Fe^{2+} and Mn^{2+}, in addition to the dehydroxylation process, for the initial stages E_1=30 –40 kJ mol^{-1}, E_{1a}=170±20 kJ mol^{-1}. But for the final stage the E value is similar to that of micas without Fe^{2+} and Mn^{2+}, namely E_2~380±40 kJ mol^{-1}.

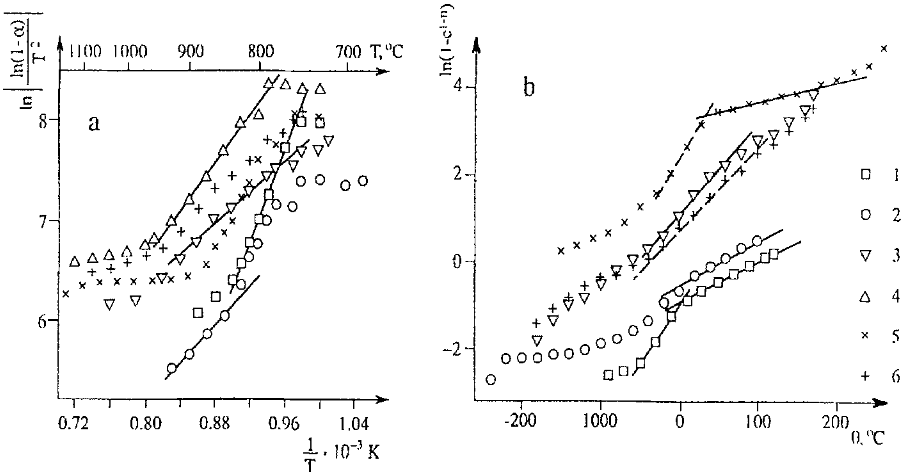

Fig. 2 Experimental TG data in accordance with Coats-Redfern (a) and Horowitz-Metzger (b) models: 1 – muscovite, 2 – phengite-muscovite, 3 – muscovite which contains some Li, 4 – Li-muscovite, 5 – Al-lepidolite, 6 – lepidolite

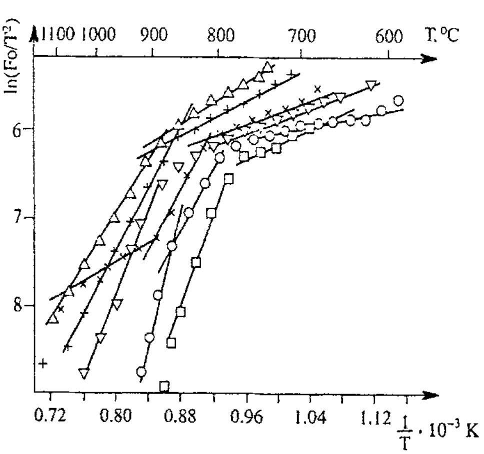

Fig. 3 Experimental TG data in accordance with the diffusion model. (For symbols see Fig. 2)

The Al-lepidolite lines (Fig. 3) have an additional stage which is connected with the loss of fluorine (E_{F}~85 kJ mol^{-1}).

Conclusion

The chemical reactions which occur during the thermal dehydroxylation [8] are not treated in this paper. Only the diffusion of the evolved products through the matrix is examined.

Figure 3 shows that the diffusion process occurs in two or three stages. The initial stage of this process is controlled by E_1~85±10 kJ mol^{-1}. From this value and the temperature interval of this stage it seems that the evolved products diffuse through a mica matrix in which only minor changes occur.

The last stage of the process is controlled by E_2~380±40 kJ mol^{-1}. This value is higher than E_1 (the temperature interval of this stage is also higher) and consequently it seems that the evolved products diffuse through a more compact matrix. At this stage a great part of the mica has already been dehydroxylated and transformed into meta-mica which contains spinel-like products and an amorphous phase [9].

Lepidolite, which contains fluorine, is characterized by a diffusion stage with E_{F}~85 kJ mol^{-1}. No similar stage is obtained for the other micas, and therefore this stage is attributed to the evolution of fluorine. From the value of the activation energy it seems that the diffusion of fluorine occurs through a non-structured material. This is in agreement with the fact that at the corresponding temperature the mica has lost its structure [9].

* * *

Part of this work was carried out in the Institute of Geochemistry of the USSR Academy Science (Irkutsk). I wish to thank Dr. S. B. Brandt for helpful discussions.

I am pleased to express my gratitude to Prof. S. Yariv for his important comments.

I am grateful to the Ministry of Absorption of the Government of Israel for financial support of this work.

References

1 M. E. Brown, D. Dollimore and A. K. Galway, in C. H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980.
2 W. W. Wendlandt, Thermal Analysis, J. Wiley & Sons, 3rd ed., New York 1986.
3 J. Madarász, G. Pokol, C. Novák, H. Moselhy and S. Gál, J. Thermal Anal., 40 (1993) 1367.
4 P. H. Fong, S. P. Wong and D. T. Y. Chen, Proc. of the 6th International Conference on Thermal Analysis (Ed. by H. G. Wiedemann), Vol. 1, 1980, p. 133.
5 G. Várhegyi, P. Szabó and F. Till, Thermochim. Acta, 92 (1985) 141.
6 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
7 A. V. Coats and J. P. Redfern, Nature, 201 (1964) 4914.

8 W. A. Addison, G. H. Neal and J. H. Sharp, J. Chem. Soc., 4 (1962) 1472.
9 E. K. Vasilyev and I. L. Lapides, Kristall und Technik, 15 (1980) 231.
10 I. L. Lapides, J. Thermal Anal., 42 (1994) 197.
11 A. Glasner, I. Pelly and M. Stainberg, J. Inorg. Nucl. Chem., 31 (1969) 3395.
12 Y. Sears and M. Stainberg, J. Catalysis, 11 (1968) 25.
13 M. Stainberg and D. Shamir, Thermochim. Acta, 84 (1985) 349.
14 A. V. Luikov, Theory of the Heat Transfer. Moskva 1967 (In Russian).
15 G. G. Goles, R. A. Fish and F. Anders, Geoch. Cosmoch. Acta, 19 (1960) 177.
16 P. Murrey and J. White, Trans. Brit. Ceram. Soc., 54 (1955) 151, 204.
17 G. J. Dienes, Phys. Rev., 91 (1953) 1283.