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THE CORRECTIONAL KINETIC EQUATION FOR THE PEAK TEMPERATURE IN THE DIFFERENTIAL THERMAL ANALYSIS

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The peak temperature (T_p) and different temperature (ΔT) are the basic information in the differential thermal analysis (DTA). Considering the kinetic relation and the heat equilibrium in DTA, a correctional differential kinetic equation (containing T_p and ΔT parameter) is proposed. In the dehydration reaction of $CaC_2O_4 \cdot H_2O$, the activation energy calculated from the new equation showed some smaller than that from Kissinger equation, but some bigger than that from Piloyan equation.

Keywords: *activation energy, kinetic equation, thermal analysis*

Introduction

In the differential thermal analysis (DTA), Kissinger equation [1] is a classic and widely applied kinetic equation [2–7], Kissinger equation [1] may be described:

$$\ln\frac{\beta}{T_p^2}=\ln C_1-\frac{E}{RT_p} \tag{1}$$

where $C_1=AR/E[-\mathrm{d}f(\alpha)/\mathrm{d}\alpha]_{\alpha_p}$. When α_p is a constant, the value of $[\mathrm{d}f(\alpha)/\mathrm{d}\alpha]_{\alpha_p}$ is also a constant. But, Kissinger considered only the kinetic relation in DTA, and neglected the heat conduction in DTA. In other words, there is not the parameter of ΔT_p in Kissinger equation.

Piloyan *et al.* [8] have ever proposed an equation,

$$\ln\Delta T=\ln C_2-\frac{E}{RT} \tag{2}$$

where $C_2=ASf(\alpha)$. The advantage of Piloyan equation is that the activation energy can be evaluated by a curve of DTA. Equation (2) can be rewritten as below:

$$\ln\left[\frac{\Delta T}{f(\alpha)}\right]=\ln C_3-\frac{E}{RT} \tag{3}$$

where $C_3=AS$. The value of α becomes big with the increase of ΔT, namely $f(\alpha)$ is not a constant. So Piloyan equation is a shortcoming.

Our work aim to a kinetic equation related kinetic relation and heat equilibrium in DTA.

Theory

In the linear heating process, the kinetic equation for a chemical reaction can be described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}e^{-\frac{E}{RT}}f(\alpha) \tag{4}$$

where α is the degree of conversion, A is the pre-exponential factor, β is the heating rate, E is the activation energy; R is the gas constant, T is the temperature in Kelvin, $f(\alpha)$ is the reaction mechanism function.

At the peak temperature of the thermal analytic curves, Eq. (4) can be expressed as:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_p=\frac{A}{\beta}e^{-\frac{E}{RT_p}}f(\alpha_p) \tag{5}$$

Take the logarithm of the Eq. (5),

$$\ln\beta\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_p=\ln A+\ln f(\alpha_p)-\frac{E}{RT_p} \tag{6}$$

Kissinger, Ozawa, Dollimore, Popescu, Segal and so on [1, 9–14] have proved and agreed with the point that the degree of conversion (α_p) at the peak temperature is a constant or quasi-constant under various heating rate, and is not related to the heating rate (β), especially Gao *et al.* who do more detailed theoretic analysis which is appropriate for most of the reaction mechanisms [12].

In the linear heating process, the values of α_p is a constant at different heating rate, so $f(\alpha_p)$ is also a constant, that is $\ln f(\alpha_p)$=constant. So the Eq. (6) can be converted as below:

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$$\ln\beta\left(\frac{d\alpha}{dT}\right)_p=\ln C-\frac{E}{RT_p}\qquad(7)$$

where $C=\ln Af(\alpha_p)$. Apparently, this is a special example in Friedman equation [15].

On the basis of heat equilibrium principle, the heat equilibrium in TA can be described as below [16]:

$$d\alpha Q=Cd\Delta T+K\Delta T dt\qquad(8)$$

where Q is the total heat of a reaction, C is the heat capacity, K is the heat conduction coefficient, ΔT is the deviation from baseline, t is time. When two sides of Eq. (8) divided by dT, it can be

$$\frac{d\alpha}{dT}=\frac{1}{Q}\left(C\frac{d(\Delta T)}{dT}+K\Delta T\frac{dt}{dT}\right)\qquad(9)$$

At peak temperature, $d(\Delta T)/dT=0$, so Eq. (9) can be rewritten as:

$$\left(\frac{d\alpha}{dT}\right)_p=\frac{K}{Q}\frac{\Delta T_p}{\beta}\qquad(10)$$

where $\beta=dT/dt$.

Taking Eq. (10) into Eq. (7), then

$$\ln\Delta T_p=\ln C_4-\frac{E}{RT_p}\qquad(11)$$

where $C_4=Af(\alpha_p)Q/K$. At the different heating rate, a set of kinetic equation can be derived:

$$\ln\Delta T_{p_1}+\frac{E}{RT_{p_1}}=\ln\Delta T_{p_2}+\frac{E}{RT_{p_2}}=\ln\Delta T_{p_3}+\frac{E}{RT_{p_3}}=\ldots\qquad(12)$$

Here, depending on the ΔT_p and T_p at different heating rate, the activation energy can be calculated.

Experimental

The $CaC_2O_4\cdot H_2O$ is analytical grade. DTA was performed on a Mettler-Toledo STAR SW9.00 with selected heating rates 1–20°C min^{-1} in the range 30–300°C. The samples with masses of 10 mg were put in Alumina 30 μL pans in an atmosphere of dry nitrogen at a flow of 20 mL min^{-1}.

The activation energy calculated by Kissinger equation is 79.762 kJ mol^{-1}, the correlation coefficient is 0.9990 (Fig. 2). The activation energy calculated by the correctional kinetic equation is 63.672 kJ mol^{-1}, the correlation coefficient is 0.9981 (Fig. 3). The activation energy calculated by the Piloyan equation is 32.102 kJ mol^{-1}, the correlation coefficient is 0.9809 (Fig. 4).

Table 1 The T_p and ΔT_p of curve peak at different heating rates of dehydration of $CaC_2O_4\cdot H_2O$

	Heating rate/K min^{-1}				
	20	10	5	2	1
T_p/°C	190.0	175.2	162.8	145.6	136.3
ΔT_p/°C	6.6	4.2	2.7	1.2	0.8

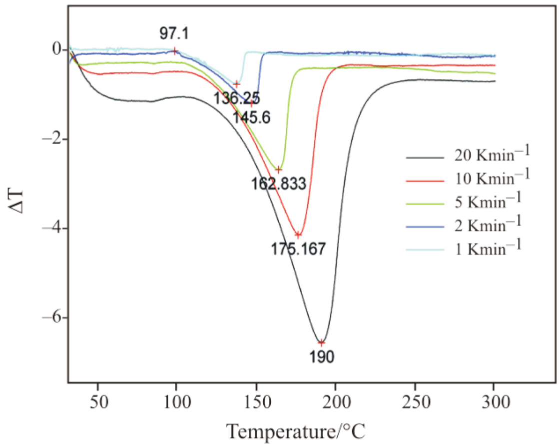

Fig. 1 The $T\sim\Delta T$ curve of dehydration of $CaC_2O_4\cdot H_2O$

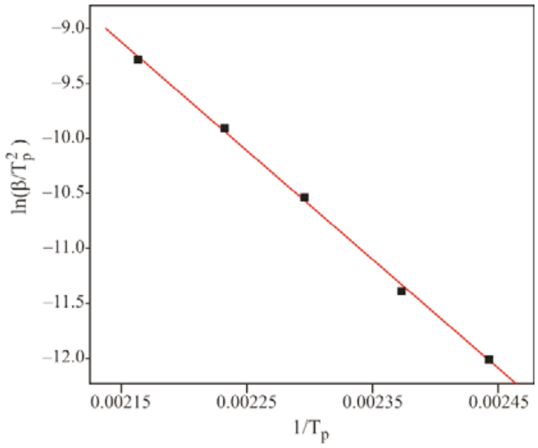

Fig. 2 The $1/T_p\sim\ln(\beta/T_p^2)$ curve based on Kissinger equation

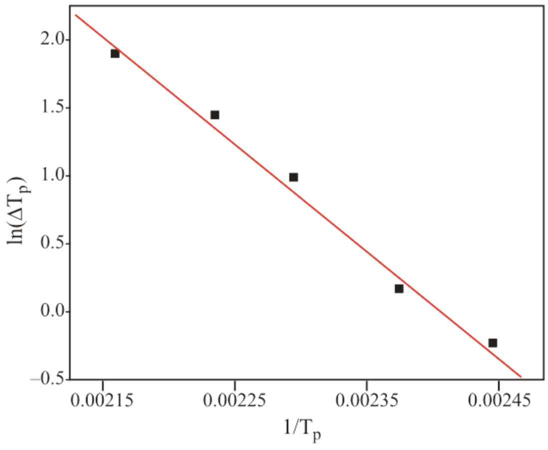

Fig. 3 The $1/T_p\sim\ln(\Delta T_p)$ curve based on the correctional kinetic equation (Eq. (8))

Table 2 The *T* and ΔT of dehydration of $CaC_2O_4\cdot H_2O$ at 20 K min^{-1}

T	100	110	120	130	140	150	160	170	180
ΔT	1.050	1.087	1.250	1.552	2.032	2.693	3.571	4.615	5.784

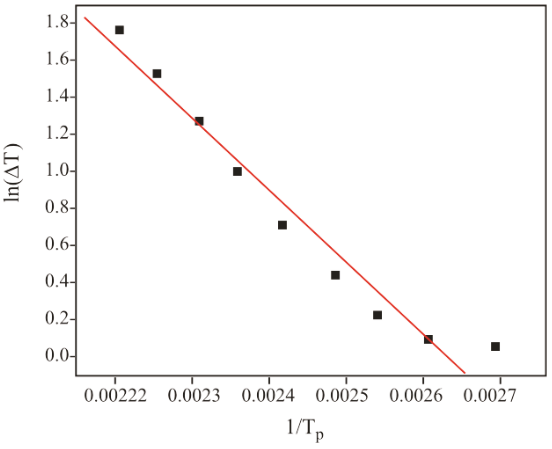

Fig. 4 The $1/T\sim\ln(\Delta T)$ curve based on the Piloyan equation at 20 K min^{-1}

Conclusions

- The curve of DTA is a curve of $\Delta T\sim T$, namely the change of ΔT with *T* may be obtained. Hence, an accurate kinetic equation from the curve of DTA should contain two parameters, ΔT and *T*.
- Considering the kinetic relation and heat equilibrium in DTA, a corrective Kissinger equation is proposed. This is a function contained T_p and ΔT.
- In the dehydration reaction of $CaC_2O_4\cdot H_2O$, the activation energy calculated from the new equation showed some smaller than that from Kissinger equation, but some bigger than that from Piloyan equation.

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