Thermochimica Acta, 223 (1993) 101–108
Elsevier Science Publishers B.V., Amsterdam

Reduced equations to estimate kinetic parameters from non-isothermal TG–DTG or DSC curves

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(Received 23 December 1992; accepted 22 January 1993)

Abstract

Reduced equations are derived in order to estimate kinetic parameters from non-isothermal TG–DTG or DSC curves

$$\frac{E}{RT_{\mathrm{m}}^2}+\frac{A}{\phi}f'(\alpha_{\mathrm{m}})\mathrm{e}^{-E/RT_{\mathrm{m}}}=0$$

$$\frac{E}{RT_{\mathrm{i}}^2}+\frac{3A}{\phi}f'(\alpha_{\mathrm{i}})\mathrm{e}^{-E/RT_{\mathrm{i}}}-\frac{2}{T_{\mathrm{i}}}=0$$

The validity of these equations was demonstrated using data obtained for the dehydration process of calcium oxalate monohydrate.

THEORY AND DERIVATION

Under non-isothermal conditions, for the solid state thermal decomposition reaction

$$\mathrm{A(s)} \rightarrow \mathrm{B(s)} + \mathrm{C(g)}$$

the generally accepted kinetic equation is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\phi}\mathrm{e}^{-E/RT}f(\alpha) \tag{1}$$

where α is the fractional decomposition, T the absolute temperature (K), $\mathrm{d}\alpha/\mathrm{d}T$ the reaction rate, A the pre-exponential Arrhenius factor, ϕ the heating rate in K min^{-1}, E the apparent activation energy (kJ mol^{-1}), R the gas constant in kJ mol^{-1} K^{-1} and $f(\alpha)$ the differential mechanism function.

Differentiation of eqn. (1) with respect to T gives

$$\frac{\mathrm{d}(\mathrm{d}\alpha/\mathrm{d}T)}{\mathrm{d}T}=\frac{A}{\phi}f(\alpha)\mathrm{e}^{-E/RT}\left[\frac{E}{RT^2}+\frac{A}{\phi}f'(\alpha)\mathrm{e}^{-E/RT}\right] \tag{2}$$

where $f'(\alpha)$ is the differentiation of $f(\alpha)$ with respect to α.

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At the point of the maximum of the DTG curve

$$\left[\frac{\mathrm{d}(\mathrm{d}\alpha/\mathrm{d}T)}{\mathrm{d}T}\right]_{T=T_\mathrm{m},\alpha=\alpha_\mathrm{m}}=0$$

Then

$$\frac{E}{RT_\mathrm{m}^2}+\frac{A}{\phi}f'(\alpha_\mathrm{m})\mathrm{e}^{-E/RT_\mathrm{m}}=0 \tag{3}$$

where the subscript m indicates the point of maximum transformation rate of the DTG curve.

Differentiation of eqn. (2) with respect to T gives

$$\frac{\mathrm{d}^2(\mathrm{d}\alpha/\mathrm{d}T)}{\mathrm{d}T^2}=Af(\alpha)\mathrm{e}^{-E/RT}\left\{\frac{E}{RT^2}\left(\frac{E}{RT^2}-\frac{2}{T}\right)+\frac{A}{\phi}\frac{3E}{RT^2}f'(\alpha)\mathrm{e}^{-E/RT}\right.$$
$$\left.+\left(\frac{A}{\phi}\right)^2[(f'(\alpha))^2+f(\alpha)f''(\alpha)]\mathrm{e}^{-2E/RT}\right\} \tag{4}$$

At the point of inflection of the DTG curve

$$\left[\frac{\mathrm{d}^2(\mathrm{d}\alpha/dT)}{\mathrm{d}T^2}\right]_{T=T_\mathrm{i},\alpha=\alpha_\mathrm{i}}=0$$

Then

$$\frac{E}{RT_\mathrm{i}^2}\left(\frac{E}{RT_\mathrm{i}^2}-\frac{2}{T_\mathrm{i}}\right)+\frac{A}{\phi}\frac{3E}{RT_\mathrm{i}^2}f'(\alpha_\mathrm{i})\mathrm{e}^{-E/RT_\mathrm{i}}$$
$$+\left(\frac{A}{\phi}\right)^2[(f'(\alpha_\mathrm{i}))^2+f(\alpha_\mathrm{i})f''(\alpha_\mathrm{i})]\mathrm{e}^{-2E/RT_\mathrm{i}}=0 \tag{5}$$

where subscript i indicates the point of inflection of the DTG curve.

The final term of eqn. (5) can be neglected, then

$$\frac{E}{RT_\mathrm{i}^2}+\frac{3A}{\phi}f'(\alpha_\mathrm{i})\mathrm{e}^{-E/RT_\mathrm{i}}-\frac{2}{T_\mathrm{i}}=0 \tag{6}$$

The above derivations yield the reduced equations, eqns. (3) and (6). By introducing the values of ϕ, T_m, T_i, $f'(\alpha_\mathrm{m})$ and $f'(\alpha_\mathrm{i})$ into the reduced simultaneous equations eqns. (3) and (6), the corresponding values of the apparent activation energy E and the pre-exponential Arrhenius factor A may be determined. The reduced equations are equally suitable for non-isothermal TG–DTG and DSC curves. These equations are much simpler than those reported in the literature [1].

EXPERIMENTAL

Samples

Calcium oxalate monohydrate was used in this study. The experiments were performed using analytical reagent grade chemicals.

TG–DTG experimental equipment and conditions

Thermogravimetric analysis of $CaC_2O_4 \cdot H_2O$ was performed on a Perkin-Elmer model TGS-2, with a nitrogen flow rate of 20 ml min^{-1}, in the temperature range 40–400°C and with a linear heating rate of 10.00°C min^{-1}. The amount of sample used was 6.0658 mg.

DSC experimental equipment and conditions

DSC analysis of $CaC_2O_4 \cdot H_2O$ was carried out using a Perkin-Elmer DSC-2C differential scanning calorimeter and 3600 data station, under a nitrogen atmosphere flowing at 20 ml min^{-1} and a heating rate of 10.00°C min^{-1}. The amount of sample used was 1.18 mg.

The reliability of the temperature and the calorimetric systems was monitored in the present experiment by measuring the melting point and the heat of fusion of indium under nitrogen atmosphere (20 ml min^{-1}) at a heating rate of 10.00°C min^{-1}. The measured values were 429.5 K and 3.28 kJ mol^{-1}, which are consistent with the literature values of 430 K and 3.26 kJ mol^{-1} [2].

RESULTS AND DISCUSSION

The validity of the obtained reduced equations, eqns. (3) and (6), was demonstrated by analysing the kinetics of the dehydration of calcium oxalate monohydrate from its TG–DTG and DSC curves, see Figs. 1 and 2.

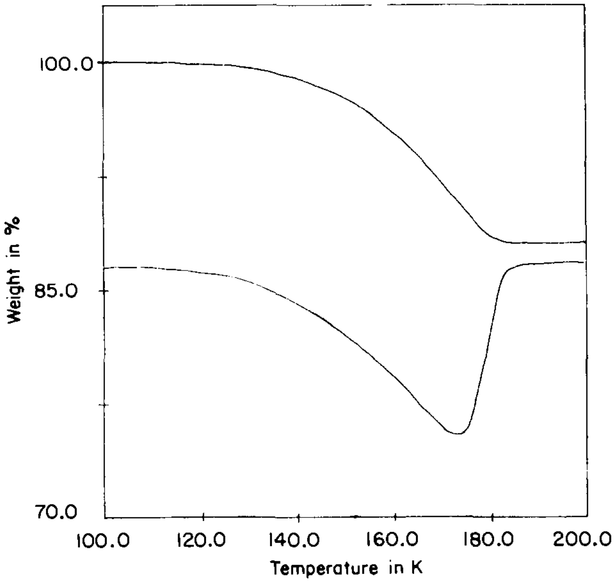

Fig. 1. The TG–DTG curves of the dehydration process of $CaC_2O_4 \cdot H_2O$.

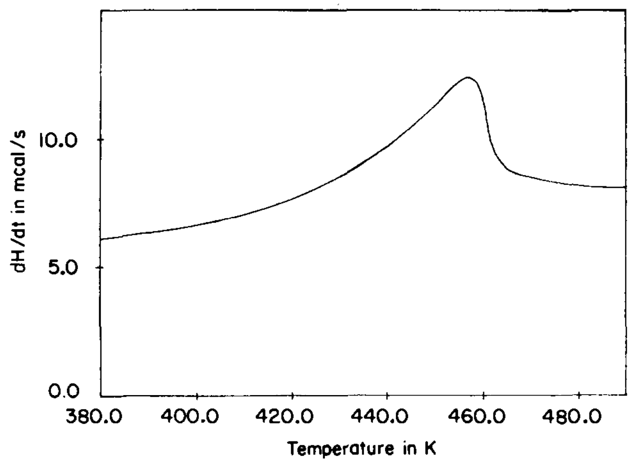

Fig. 2. The DSC curve of the dehydration process of $CaC_2O_4 \cdot H_2O$.

The original data determined from the TG–DTG curve are listed in Table 1.

For the TG–DTG curve, Narahari Achar et al.'s differential equation [3] and the Coats–Redfern integral equation [4] were used to analyse the non-isothermal dehydration. The integral and differential equations are

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\phi E} - \frac{E}{RT} \tag{7}$$

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\right] = \ln A - \frac{E}{RT} \tag{8}$$

Equation (7) is the reduced formula [5]. The selected possible forms of $g(\alpha)$ and $f(\alpha)$ are listed in Table 2. Using the possible forms of $g(\alpha)$ and $f(\alpha)$, the data in Table 1 were analysed using eqns. (7) and (8). For eqns. (7) and

TABLE 1

Data for the dehydration process of $CaC_2O_4 \cdot H_2O$ determined by TG–DTG

No.	T/K	α	$\mathrm{d}\alpha/\mathrm{d}t$
1	413.15	0.008	0.211
2	423.15	0.202	0.386
3	428.15	0.287	0.509
4	433.15	0.388	0.614
5	438.15	0.516	0.754
6	443.15	0.665	0.912
7	448.15	0.836	0.947
8	451.15	0.926	0.965
9	453.15	0.975	0.404

TABLE 2

The kinetic functions used in the analysis

Function no.	Function form		
	Integral form $g(\alpha)$	Differential form $f(\alpha)$	$f'(\alpha)$
1	α^2	$1/(2\alpha)$	$-1/(2\alpha^2)$
2	$\alpha + (1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	$-(1-\alpha)^{-1}[\ln(1-\alpha)]^{-2}$
3	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$	$-0.5(1-\alpha)^{-4/3}[(1-\alpha)^{-1/3}-1]^{-2}$
4	$[1-(1-\alpha)^{1/3}]^2$	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$-(1-\alpha)^{-1/3}[1-(1-\alpha)^{1/3}]^{-1}-0.5[1-(1-\alpha)^{1/3}]^{-2}$
5	$[(1-\alpha)^{1/3}-1]^2$	$1.5(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$(1+\alpha)^{-1/3}[(1+\alpha)^{1/3}-1]^{-1}-0.5[(1+\alpha)^{1/3}-1]^{-2}$
6	$[1/(1-\alpha)^{1/3}-1]^2$	$1.5(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$-2(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}-0.5(1-\alpha)^{-1/3}-1]^{-2}$
7	$-\ln(1-\alpha)$	$1-\alpha$	-1
8	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$0.5[-\ln(1-\alpha)]^{-2/3}-1.5[-\ln(1-\alpha)]^{1/3}$
9	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{-1/2}-2[-\ln(1-\alpha)]^{1/2}$
10	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$2[-\ln(1-\alpha)]^{-1/3}-3[-\ln(1-\alpha)]^{2/3}$
11	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$3[-\ln(1-\alpha)]^{-1/4}-4[-\ln(1-\alpha)]^{3/4}$
12	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	$-(1-\alpha)^{-1/2}$
13	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	$-2(1-\alpha)^{-1/3}$
14	α	1	0
15	$\alpha^{1/2}$	$2\alpha^{1/2}$	$\alpha^{-1/2}$
16	$\alpha^{1/3}$	$3\alpha^{2/3}$	$2\alpha^{-1/3}$
17	$\alpha^{1/4}$	$4\alpha^{3/4}$	$3\alpha^{-1/4}$
18	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$	$-2(1-\alpha)$
19	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$	$-3(1-\alpha)^{1/2}$

TABLE 3

Results of analysis of the thermal dehydration data of $CaC_2O_4 \cdot H_2O$ in Table 1 using the integral equation eqn. (7) and the differential equation, eqn. (8)

Function no.	Integral method			Differential method		
	E/kJ mol^{-1}	ln A/s^{-1}	r	E/kJ mol^{-1}	ln A/s^{-1}	r
1	176.94	43.10	0.9927	135.83	32.63	0.9422
2	199.72	49.08	0.9979	181.86	45.13	0.9889
3	210.18	50.62	0.9991	203.76	49.88	0.9966
4	232.09	56.99	0.9992	244.11	61.41	0.9962
5	159.15	35.60	0.9888	110.56	23.05	0.9091
6	312.79	30.35	0.9842	365.15	95.99	0.9701
7	130.89	31.45	0.9942	164.80	41.99	0.9717
8	84.86	18.44	0.9939	118.77	29.01	0.9574
9	61.84	11.84	0.9935	95.75	22.44	0.9431
10	38.82	5.09	0.9928	72.73	15.75	0.9166
11	27.32	1.59	0.9919	61.22	12.32	0.8937
12	104.46	22.97	0.9994	104.28	24.01	0.9905
13	112.44	24.92	0.9992	124.45	29.37	0.9884
14	84.86	17.83	0.9921	43.76	7.41	0.7400
15	38.83	4.78	0.9904	−2.28	−5.55	0.0633
16	23.48	0.19	0.9881	−17.62	−10.05	0.4525
17	15.81	−2.25	0.9851	−25.30	−12.38	0.5952
18	205.91	53.30	0.9536	285.84	76.58	0.9303
19	53.31	10.12	0.8207	225.32	58.59	0.9476

(8), the kinetic analyses were completed by the linear least-squares method on a computer. The results are shown in Table 3.

The results in Table 3 clearly show that the values of E and A from the two methods are approximately the same and that the linear correlation coefficient is highest when the probable mechanism function is function no. 12 in Table 2, which, it can be concluded, is the probable mechanism function of the dehydration process of $CaC_2O_4 \cdot H_2O$. The E and A values for this function are listed in Table 5.

The kinetics was also analysed by the present method. The values of T_m, T_i, α_m and α_i from the TG–DTG and DSC curves are shown in Table 4.

By introducing all the forms of $f'(\alpha)$ listed in Table 2 and the values of ϕ, T_m, T_i, α_m and α_i obtained from the TG–DTG or DSC curves into eqns. (3) and (6), the corresponding values of E and A may be determined using a computer. The results are shown in Table 4. The values of E and A are in agreement with those calculated by the Narahari Achar et al. and Coats–Redfern methods when the probable mechanism is function No. 12 (Table 2).

A comparison between the results obtained in this work and those reported in the literature is given in Table 5.

TABLE 4

Calculated values of the kinetic parameters for the thermal dehydration of $CaC_2O_4 \cdot H_2O$ using the reduced equations, eqns. (3) and (6), deduced in this paper

Function no.	TG–DTG		DSC	
	$T_m = 415.18$ K $T_i = 444.15$ K	$\alpha_m = 0.926$ $\alpha_i = 0.697$	$T_m = 456.58$ K $T_i = 446.00$ K	$\alpha_m = 0.776$ $\alpha_i = 0.430$
	E/kJ mol^{-1}	ln A/s^{-1}	E/kJ mol^{-1}	ln A/s^{-1}
1	392.03	101.80	345.48	87.79
2	294.37	74.25	334.44	83.98
3	305.81	75.89	335.85	82.87
4	374.90	94.92	345.40	85.58
5	394.98	100.42	346.40	85.86
6	650.23	170.74	416.23	105.31
7	259.74	65.58	175.21	42.07
8	157.54	37.24	42.77	5.49
9	100.44	21.20	10.19	−4.73
10	46.66	5.62	4.10	−7.54
11	29.10	0.14	1.65	−9.30
12	103.33	21.66	105.22	22.38
13	153.23	35.10	128.01	28.13
14	–	–	–	–
15	292.63	–	220.94	–
16	281.66	–	205.66	–
17	276.17	–	198.02	–
18	583.47	154.60	319.60	81.52
19	423.46	109.91	247.47	61.10

TABLE 5

A comparison between the results obtained in this work and those reported in the literature

		E/kJ mol^{-1}	A/s^{-1}	$f(\alpha)$
This work				
Integral method	(TG–DTG)	104.46	9.46×10^9	$2(1-\alpha)^{1/2}$
Differential method	(TG–DTG)	104.28	2.68×10^{10}	$2(1-\alpha)^{1/2}$
Reduced equations	(TG–DTG)	103.33	2.55×10^9	$2(1-\alpha)^{1/2}$
Reduced equations	(DSC)	105.22	5.22×10^9	$2(1-\alpha)^{1/2}$
Ref. 6		92.05	–	$1-\alpha$
Ref. 7		118.00	6.60×10^{11}	$2(1-\alpha)^{1/2}$

CONCLUSIONS

Using the reduced equations obtained in this paper, one can estimate the values of the apparent activation energy E and the pre-exponential Arrhenius factor A from a single non-isothermal TG–DTG or DSC curve. These equations can not only determine the kinetic parameters but can also be helpful in discrimination of the probable mechanism function.

REFERENCES

1 Z.-Q. Yang, R.-Z. Hu and Y. Xie, Thermochim. Acta, 195 (1992) 157.
2 Yu-Zeng Li, Thermal Analysis, Qinghua University Press, Beijing, 1987, p. 241 (in Chinese)
3 B.N. Narahari Achar, G.W. Bridley and J.H. Sharp, Proc. Int. Clay Conf., Vol. 1, Jerusalem, 1966, p. 67.
4 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
5 A.B. Phadnis and V.V. Deshpande, Thermochim. Acta, 62 (1983) 361.
6 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
7 R. Lozano, J. Roman and F. de Jesus, Thermochim. Acta, 143 (1989) 93.