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Note

Determination of kinetic parameters from thermogravimetric data

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The method described enables the determination of the kinetical parameter, activation energy, and the frequency factor with the degree of error generally being below one percent. The data on which the calculations are to be based has to be prepared in form of combined measurement couples as used in electronic data processing.

MATHEMATICAL PROCEDURE

In principle, the kinetic parameter is calculated by means of the method of least squares. For this purpose, the rate of chemical change has to be written in the form of a differential equation and the transition from differentials to finite differences, as feasible under certain conditions*, has to be made.

$$\frac{\mathrm{d}a}{\mathrm{d}t} \cong \frac{\Delta a}{\Delta t} = \mathrm{k} \cdot \mathrm{f}(a) \qquad k = Z \cdot \exp(-E/RT)$$

For a satisfactory kinetical parameter, the sum of the least squares E and Z has to provide a minimum value.

If we substitute

$\mathrm{f}(a) = (1 - a)^n$, where n = order of reaction

for $\mathrm{f}(a)$, then we obtain the following conditions for determining the values required:

$$\sum_i \left[\frac{\Delta a_i}{\Delta t_i} - Z \cdot \exp(-E/RT_i) \cdot (1 - a_i)^n\right]^2 = \min = \sum A_i^2$$

These conditions are only fulfilled if it is valid that:

$$\frac{\partial}{\partial n}(\sum A_i^2) = 0;\ \frac{\partial}{\partial E}(\sum A_i^2) = 0);\ \frac{\partial}{\partial Z}(\sum A_i^2) = 0$$

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* The conditions are a sufficiently small distance between the points of measurement. 80 to 100 equidistant points of measurement have proved to be sufficient.

Thus we obtain the following four equations:

$$\sum_i \left[\frac{\Delta a_i}{\Delta t_i} - Z\cdot\exp(-E/RT_i)\cdot(1-a_i)^n\right]^2 = \min \qquad (1)$$

$$\sum_i [A_i\cdot n\cdot Z\cdot(1-a_i)^{n-1}\cdot\exp(-E/RT_i)] = 0 \qquad (2)$$

$$\sum_i [A_i\cdot(Z/RT_i)\cdot(1-a_i)^n\cdot\exp(-E/RT_i)] = 0 \qquad (3)$$

$$\sum_i [-A_i(1-a_i)^n\cdot\exp(-E/RT_i)] = 0 \qquad (4)$$

Using the equation (4) the frequency factor Z can easily be determined:

$$Z = \frac{\sum_i \frac{\Delta a_i}{\Delta t_i}(1-a_i)^n\cdot\exp(-E/RT_i)}{\sum_i [(1-a_i)^n\cdot\exp(-E/RT_i)]^2}$$

By varying the coefficients E and n, the minimum value of the first equation can be calculated and thus also the required parameters n, E and Z.

TESTING THE METHOD

In order to test the method, the predetermined reaction curves, as estimated by applying Sestak's formula, were analysed.

Sestak's[7] formula: $x = E/RT$

$$p(x) = \frac{\exp(-x)}{x}\;\frac{674.567 - 57.412x - 6.055x^2 - x^3}{1699.066 + 841.655x + 49.313x^2 - 8.022x^3 - x^4}$$

TABLE 1

TESTING THE METHOD TO DETERMINE THE KINETICAL PARAMETER WITH THEORETICALLY PREDETERMINED TG-CURVES (calculated with Sestak's formula)

Results calculated		*Results obtained*	
E(kcal mol⁻¹ K⁻¹)	*ln Z*	*E(kcal mol⁻¹ K⁻¹)*	*ln Z*
15.00	10.60	15.05	10.67
18.00	13.30	17.99	13.36
19.75	13.74	19.73	13.73
14.25	12.16	14.28	12.22

Testing the reproducibility of the results concerning energy of activation and frequency factor.

TABLE 2

REACTION INVESTIGATED: CALCIUM OXALATE-DEHYDRATION
$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$
(order of reaction: $n = 0.5$)

E(kcal mol⁻¹ K⁻¹)	v_iv_i	*ln Z*	v_iv_i
19.82	0.005	13.88	0.020
19.84	0.008	13.90	0.026
19.69	0.004	13.79	0.002
19.84	0.008	13.88	0.020
19.79	0.002	13.81	0.005
19.60	0.022	13.61	0.017
19.62	0.017	13.67	0.005
19.87	0.014	13.71	0.001
19.80	0.002	13.64	0.010
19.60	0.022	13.47	0.073
19.78	0.001	13.73	0.000
19.73	0.000	13.75	0.000
19.75 mean value		13.74	
(0.76%) 0.15 maximum deviation		0.27 (1.07%)	
(0.50%) 0.10 standard deviation		0.13 (0.93%)	

TABLE 3

REACTION INVESTIGATED: ETTRINGITE-DEHYDRATION
$6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 30H_2O \rightarrow 6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 6H_2O + 24H_2O$
(order of reaction: $n = 1$)

E(kcal mol⁻¹ K⁻¹)	v_iv_i	*ln Z*	v_iv_i
16.38	0.035	14.48	0.010
16.08	0.013	14.42	0.002
16.15	0.002	14.36	0.000
16.48	0.082	14.59	0.044
16.16	0.001	14.41	0.001
16.22	0.001	14.33	0.002
16.10	0.009	14.36	0.000
16.14	0.003	14.23	0.022
16.01	0.034	14.32	0.004
16.01	0.034	14.18	0.040
16.30	0.011	14.33	0.002
16.19 mean value		14.38	
(1.79%) 0.29 maximum deviation		0.21 (1.46%)	
(0.90%) 0.15 standard deviation		0.12 (0.83%)	

As can be seen from the results presented in Table 1 the deviations from the mean value lie only within the range of the second decimal point.

The reproducibility of the measurement of the kinetical parameter was tested by using 12 series of measurements with calcium oxalate $CaC_2O_4 \cdot H_2O$ and ettringite syn. $6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 30H_2O$, respectively. The results, as presented in Tables 2 and 3, show that measurements of the kinetical parameter with a standard deviation of less than 1% are quite feasible.

EXPERIMENTAL PROCEDURE

The relevant thermogravimetric measurements were derived by using a Mettler thermoanalyser. 200-mg samples were used. The heat increase was kept to 2°C min^{-1}. The data was processed in a mini computer (CAI) attached. It was also used for the numerical calculations.

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