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COMPUTATION OF ACTIVATION ENERGY SPECTRUM — A NEW APPROACH

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ABSTRACT

A new and convenient method for determination of the activation energy, E as a function of heating rate and sample mass has been proposed from thermogravimetric data. The basic equation for the calculation of E depends on the relation between the reciprocal of activation energy and logarithm of heating rate ϕ in the case of certain reactions. This method predicts the activation energy at any intermediate heating rate from two known values of E and ϕ. A new correlation between sample mass m, E and ϕ is also obtained, which can be represented by the equation

$$\frac{1}{E} = \mathrm{a}_1 + \mathrm{a}_2 m + (\mathrm{b}_1 + \mathrm{b}_2 \ln m) \ln \phi$$

where a_1, a_2 and b_1, b_2 are empirical constants. The calculated values of E are comparable with those from TG experiments for the dehydration of zinc oxalate dihydrate.

INTRODUCTION

It is well established that procedural factors such as heating rate, sample mass, particle size, atmosphere, etc., have a pronounced effect on the shape of thermoanalytical curves and consequently the kinetic parameters are also affected [1–7]. Several attempts have been made to correlate the kinetic parameters and procedural factors quantitatively [8–13], but no attempt has been made to calculate the activation energy at an intermediate heating rate, ϕ, for a constant sample mass or for a constant heating rate at any sample mass knowing the values of E at any two heating rates ϕ_1 and ϕ_2. In this communication, we are introducing a new simple method for calculating the activation energy at intermediate heating rates from thermogravimetric data.

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EXPERIMENTAL

The sample of $ZnC_2O_4 \cdot 2H_2O$ used for the present investigation has the same purity and degree of subdivision as in our previous studies [12,13]. TG experiments were carried out in a nitrogen atmosphere using a Du Pont 990 Thermal Analyser system with 951 Thermogravimetric Analyser. Five sample masses (5, 10, 15, 20 and 25 mg) and seven heating rates for each sample mass (1, 2, 5, 10, 20, 50 and 100°C $\min^{-1}$) were used. Activation energy was computed using a CDC computer with a FORTRAN IV program.

RESULTS AND DISCUSSION

Activation energy values were computed using the Coats–Redfern method [14] for dehydration of $ZnC_2O_4 \cdot 2H_2O$ from the 35 sets of TG curves and the results are given in Table 1. It can be seen (Table 1) that the E values decrease systematically with increase in sample mass horizontally and decrease with increase in heating rate vertically. Similar observations were made earlier also [11]. The systematic trend makes the data amenable for quantitative correlations.

Theoretical

For a constant sample mass, the linear variation of the reciprocal of activation energy versus logarithm of the heating rate may be represented as

$$\frac{1}{E} = \mathrm{a} + \mathrm{b} \ln \phi \qquad (1)$$

where a and b are constants. Let $E_{(\max)}$ be the maximum E value at a minimum heating rate, $\phi_{(\min)}$ and $E_{(\min)}$ be the minimum activation energy

TABLE 1

Values of E (kcal mol^{-1}) for the dehydration of $ZnC_2O_4 \cdot 2H_2O$ from TG data

Heating rate (°C $\min^{-1}$)	Values of E for sample mass (mg):				
	5	10	15	20	25
1	60.785	57.891	54.240	45.825	43.000
2	50.000	44.999	39.654	35.500	33.500
5	40.050	34.500	31.250	28.409	26.675
10	34.000	29.400	26.500	24.349	22.750
20	29.105	26.106	23.000	21.250	19.750
50	23.955	21.861	19.775	17.886	16.725
100	21.750	19.273	17.415	16.000	15.163

TABLE 2

Comparison of calculated values of E (kcal mol^{-1}) at intermediate heating rates with experimental values

Heating rate (°C min^{-1})	Values of E for sample mass (mg):														
	5			10			15			20			25		
	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.
2	50.00	47.86	−4.28	45.00	44.48	−1.13	39.65	41.14	+3.76	35.50	35.78	+0.78	33.50	33.69	+0.57
5	40.05	37.36	−6.72	34.50	33.94	−1.62	31.25	31.19	−0.19	28.40	27.75	−2.29	26.67	26.19	−1.78
10	34.00	32.04	−5.76	29.40	28.92	−1.63	26.50	26.36	−0.57	24.34	23.72	−2.55	22.75	22.42	−1.45
20	29.10	28.04	−3.64	26.11	25.13	−3.75	23.00	22.83	−0.74	21.25	20.72	−2.49	19.75	19.60	−0.76
50	23.96	24.08	+0.50	21.86	21.42	−2.04	19.77	19.40	−1.87	17.88	17.74	−0.78	16.72	16.80	+0.48

TABLE 3

Values of slope, intercept and r from a plot of $1/E$ vs. $\ln\phi$

Sample mass (mg)	Slope (b)	Intercept (a)	r
5	6.535743×10^{-3}	0.0153699	0.9970
10	7.405934×10^{-3}	0.0170086	0.9992
15	8.272317×10^{-3}	0.0187894	0.9994
20	8.750592×10^{-3}	0.0215267	0.9993
25	9.292391×10^{-3}	0.0230213	0.9997

at the maximum heating rate, $\phi_{(\max)}$. Assume E be the activation energy at an unknown heating rate, ϕ such that $\phi_{(\min)} < \phi < \phi_{(\max)}$. Equation (1) can now be transformed into the form

$$\frac{1/E - 1/E_{(\min)}}{1/E_{(\max)} - 1/E} = \frac{\ln\phi_{(\max)} - \ln\phi}{\ln\phi - \ln\phi_{(\min)}} \tag{2}$$

E at intermediate heating rate ϕ can be calculated from eqn. (2), knowing $E_{(\min)}$, $E_{(\max)}$, $\phi_{(\min)}$ and $\phi_{(\max)}$ respectively.

Table 2 gives the values of E calculated for each sample mass at intermediate heating rates using eqn. (2). The calculated E values are comparable with the experimentally determined E values and the percentage deviations are < 5% in almost all cases.

Linear plots of $1/E$ versus $\ln\phi$ were drawn for each sample mass and the respective values of the slope, the intercept and the correlation coefficients, r, are given in Table 3. All the plots have correlation coefficients above 0.99 indicating the linearity of the fit. It is also observed that the slopes and intercepts are increasing systematically with increase in sample mass.

Variation of slope and intercept

It is found that the slope, b obtained from $1/E$ versus $\ln\phi$ plot varies linearly with $\ln m$. This relation can be represented as

$$b = b_1 + b_2 \ln m \tag{3}$$

where b_1 and b_2 are constants. The numerical values of b_1, b_2 and the corresponding correlation coefficient are given as: $b_1 = 5.289481\times10^{-3}$; $b_2 = 1.075954\times10^{-3}$; $r = 0.9930$.

The intercept, a, from Table 2 has a linear relation with m. Therefore, the equation corresponding to this is

$$a = a_1 + a_2 m \tag{4}$$

TABLE 4

Comparison of calculated values of E (kcal mol^{-1}) from eqn. (6) with experimental values

Heating rate (°C min^{-1})	Values of E for sample mass (mg):														
	5			10			15			20			25		
	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.	Expt.	Cal.	% devn.
1	60.78	65.88	+8.34	57.89	58.27	+0.66	54.24	52.24	−3.68	45.82	47.34	−3.32	43.00	43.28	−0.65
2	50.00	49.89	−0.22	45.00	44.36	−1.42	39.65	40.27	+1.56	35.50	37.00	+4.22	33.50	34.28	+2.33
5	40.05	37.77	−5.69	34.50	33.72	−2.26	31.25	30.92	−1.06	28.41	28.71	+1.05	26.68	26.88	+0.75
10	34.05	31.90	−6.30	29.40	28.53	−2.96	26.50	26.29	−0.79	24.35	24.53	+0.82	22.75	23.11	−1.58
20	29.10	27.62	−5.08	26.11	24.73	−5.28	23.00	22.87	−0.56	21.25	21.45	+0.94	19.75	20.27	+2.63
50	23.96	23.49	−1.96	21.86	21.03	−3.79	19.77	19.52	−1.26	17.89	18.37	+2.68	16.72	17.44	+4.30
100	21.75	21.05	−3.22	19.27	18.89	−1.97	17.42	17.57	+0.86	16.00	15.58	−2.62	15.16	15.77	+4.02

The numerical values of a_1, a_2 and r are as follows: $a_1 = 0.013197$; $a_2 = 3.96420 \times 10^{-4}$; $r = 0.9956$.

Hence, eqn. (1) can be rewritten as

$$1/E = a_1 + a_2 m + (b_1 + b_2 \ln m) \ln \phi \tag{5}$$

On substituting the numerical values of a_1, a_2, and b_1, b_2, eqn. (5) becomes

$$1/E = 0.013197 + (3.96420 \times 10^{-4} m) + (5.289481 \times 10^{-3} + (1.075954 \times 10^{-3} \ln m)) \ln \phi \tag{6}$$

Table 4 gives the computed values of E from eqn. (6) and the experimentally determined values of E. It is found that the E values are comparable for both the methods. The deviations of the calculated and the experimental E values are less than 5% in almost all cases, thus confirming the validity of the equation employed in this work.

CONCLUSION

The advantage of the present method is that the determination of activation energy for a given sample mass at intermediate heating rates has been simplified to a mere calculation, provided the TG data are available at any two heating rates.

The dependence of the activation energy on sample mass and heating rate has been correlated in eqn. (6). If the TG data for the sample masses at two heating rates (for each sample mass) are known, the spectrum of the activation energy for different sample masses and different heating rates can be computed for a particular reaction.

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