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Note

KINETICS FROM THERMOGRAVIMETRIC TRACES

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While working on the kinetics of the thermal decomposition of iron(II) sulphate heptahydrate using Zsakó's method [1,2], it was observed that the method can probably be simplified when dealing with a large number of mechanistic equations such as those summarised by Nair and Madhusudanan [3]. Subsequently, the method has been simplified and applied to some systems with excellent results. In principle, the simplified method involves calculation of $\bar{\delta}$ using three or four $-\log p(x)$ values and eliminates calculation of δ_{min}. The method is illustrated by considering the thermal decomposition of iron(II) sulphate heptahydrate to the monohydrate, in air. It is assumed that the reader is familiar with Zsakó's original method mentioned above.

Iron(II) sulphate heptahydrate decomposes to iron(II) sulphate monohydrate in the temperature range 403–473 K according to the equation

$$FeSO_4 \cdot 7\,H_2O \rightarrow FeSO_4 \cdot H_2O + 6\,H_2O \quad (1)$$

The kinetics and mechanism of this reaction have been determined using Zsakó's method [2], which involves calculation of δ using a large number of $-\log p(x)$ values to arrive at δ_{min} for a given mechanism, and then arriving at a minimum value of δ_{min} by repeating the procedure for various mechanisms. The equation giving the minimum value of δ_{min} is taken as that giving the correct mechanism and the corresponding E value as the correct activation energy.

In the present method, calculation of the minimum value of δ_{min} is avoided as it usually involves a large number of $-\log p(x)$ values, especially when one has no idea of the magnitude of the activation energy. Three or four $-\log p(x)$ values are chosen in the same activation energy range. The δ values are then calculated for these selected $-\log p(x)$ values, and the arithmetic mean, $\bar{\delta}$, is calculated for each mechanistic equation. The mechanistic equation which gives the minimum value of $\bar{\delta}$ is taken as the one correctly representing the mechanism. It may be stated here that the equation which gives the minimum value of δ_{min}, also gives the minimum value of $\bar{\delta}$, and this simplifies the procedure. After arriving at the mechanism, a plot of E vs. δ is made. The straight line thus obtained cuts the E axis at a value

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TABLE 1

Evaluation of the mechanism and activation energy for the reaction $FeSO_4 \cdot 7\,H_2O = FeSO_4 \cdot H_2O + 6\,H_2O$

Mechanistic eqn.	$-\log p(x)$				
	E				
	18	20	22	24	
	$\delta =$				$\bar{\delta}$
$g(\alpha) = \alpha^2$	0.2571	0.2197	0.1923	0.1880	0.2143
$g(\alpha) = \alpha + (1+\alpha)\ln(1-\alpha)$	0.3116	0.2651	0.2702	0.2042	0.2628
$g(\alpha) = [1-(1-\alpha)^{1/3}]^2$	0.3794	0.3384	0.2826	0.2573	0.3114
$g(\alpha) = (1-2/3\,\alpha)-(1-\alpha)^{2/3}$	0.3358	0.2876	0.2376	0.2178	0.2697
$g(\alpha) = -\ln(1-\alpha)$	0.0666	0.1077	0.1726	0.2380	0.1311
$g(\alpha) = [-\ln(1-\alpha)]^{1/2}$	0.2964	0.3514	0.4193	0.4534	0.3801
$g(\alpha) = [-\ln(1-\alpha)]^{1/3}$	0.3813	0.4364	0.5042	0.5352	0.4650
$g(\alpha) = (1-(1-\alpha)^{1/2}$	0.1397	0.1884	0.2537	0.2874	0.2173
$g(\alpha) = 1-(1-\alpha)^{1/3}$	0.1161	0.1635	0.2287	0.2624	0.1927

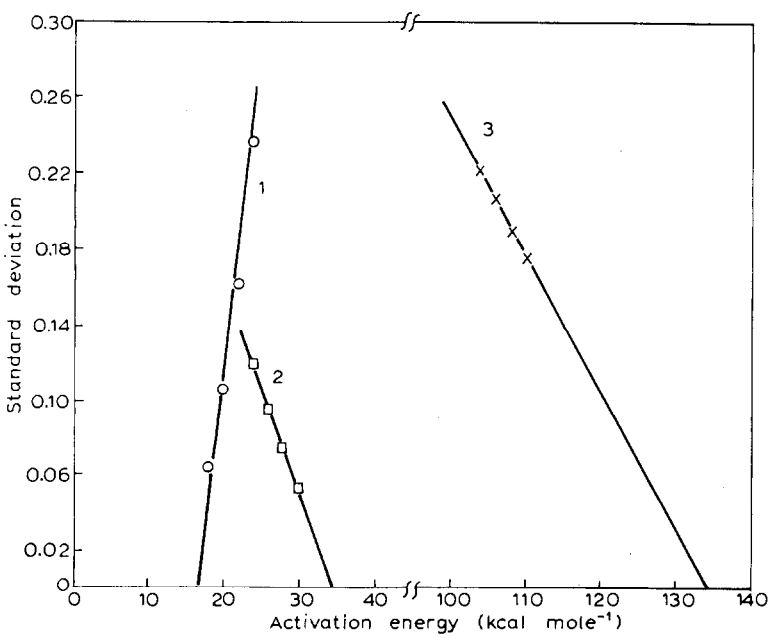

Fig. 1. Kinetics of the thermal decomposition of iron(II) sulphate heptahydrate. 1, $FeSO_4 \cdot 7\,H_2O \rightarrow FeSO_4 \cdot H_2O + 6\,H_2O$; 2, $FeSO_4 \cdot H_2O \rightarrow FeSO_4 + H_2O$; 3, $Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2\,SO_3$.

TABLE 2

Comparison of data and a summary

Reaction	Mechanistic equation		E(kcal mole^{-1})	
	Present method	Zsakó's method	Present method	Zsakó's method
$FeSO_4 \cdot 7\ H_2O \rightarrow$ $FeSO_4 \cdot H_2O + 6\ H_2O$	$-\ln(1-\alpha)$	$-\ln(1-\alpha)$	17	16(17 [a])
$FeSO_4 \cdot H_2O \rightarrow$ $FeSO_4 + H_2O$	$-\ln(1-\alpha)^{1/2}$	$-\ln(1-\alpha)^{1/2}$	35	34(35 [a])
$Fe_2O(SO_4)_2 \rightarrow$ $Fe_2O_3 + 2\ SO_3$	α^2	α^2	134	132(133 [a])

[a] Interpolated values.

corresponding to the activation energy for the reaction. Once again it may be stated that the value so obtained for the activation energy agrees with the 'interpolated' value of the original method of Zsakó. Thus the advantages of the method are: (1) the whole range of $-\log p(x)$ values need not be considered, especially when there is no prior idea of the activation energy, and (2) the method is applicable even when the activation energy value falls beyond the range of $-\log p(x)$ values tabulated by Zsakó.

Table 1 gives $\bar{\delta}$ values for various mechanistic equations. It is evident that the equation, $g(\alpha) = -\ln(1-\alpha)$, gives the minimum value of $\bar{\delta}$ value of 0.1311 and hence represents the correct mechanism. Plot 1 of Fig. 1 gives a value of 17 kcal mole^{-1} for the activation energy. Table 2 gives a comparison between the original method of Zsakó and the present approach and also provides comparative data for the reactions

$$FeSO_4 \cdot H_2O \rightarrow FeSO_4 + H_2O \quad (2)$$

$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2\ SO_3 \quad (3)$$

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