

Note

DETERMINATION OF ACTIVATION ENERGY VALUE FROM THE MAXIMUM RATE OF REACTION POINTS OBTAINED FROM NON-ISOTHERMAL EXPERIMENTS

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For a series of experiments on a given compound, the activation energy value could be determined conveniently from the maximum rate of reaction points alone. This method, however, provides a quicker and more useful way to analyse the kinetic data from those techniques where the data output is in the form of derivatives, i.e., $d\alpha/dT$.

The rate of a solid-state decomposition reaction is conventionally given by

$$d\alpha/dt = Kf(\alpha) \quad (1)$$

Where K is the specific rate constant and $f(\alpha)$ is some function of α describing the mechanism of reaction.

Considering a linear heating rate (i.e., $\beta = dT/dt$) and assuming an Arrhenius relationship for K , eqn. (1) can be expressed as

$$d\alpha/dT = \frac{A}{\beta} \exp(-E/RT)f(\alpha) \quad (2)$$

which after rearrangements and taking integrals from both sides the above equation takes the form of

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T \exp(-E/RT)dT \quad (3)$$

Where E and A are the activation energy and pre-exponential factor, respectively, and $g(\alpha)$ is a mechanism-dependent term.

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At the maximum point, the second derivative of eqn. (2) is equal to zero, thus

$$\begin{aligned} \left. \frac{d}{dT} \left(\frac{d\alpha}{dT} \right) \right|_{T_m} &= \frac{A}{\beta} \left[e^{-E/RT_m} \frac{Ef(\alpha_m)}{RT_m^2} + \left. \frac{df(\alpha)}{dT} \right|_{T_m} e^{-E/RT_m} \right] = 0 \\ &= \frac{A}{\beta} e^{-E/RT_m} \left[E/RT_m^2 f(\alpha) + \left. \frac{df(\alpha)}{dT} \right|_{T_m} \right] = 0 \end{aligned} \quad (4)$$

Now

$$\left. \frac{df(\alpha)}{dT} \right|_{T_m} = \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \left. \frac{d\alpha}{dT} \right|_{T_m} = \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \frac{A}{\beta} e^{-E/RT_m} f(\alpha)_m \quad (5)$$

Substituting eqn. (5) into eqn. (4) gives

$$\left. \frac{d}{dT} \left(\frac{d\alpha}{dT} \right) \right|_{T_m} = \frac{A}{\beta} e^{-E/RT_m} \left[E/RT_m^2 f(\alpha_m) + \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \frac{A}{\beta} e^{-E/RT_m} f(\alpha_m) \right] = 0$$

or

$$\left. \frac{d}{dT} \left(\frac{d\alpha}{dT} \right) \right|_{T_m} = \frac{A}{\beta} e^{-E/RT_m} f(\alpha_m) \left[E/RT_m^2 + \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \frac{A}{\beta} e^{-E/RT_m} \right] = 0 \quad (6)$$

For this equation to be zero, there are two possibilities: that $A/\beta e^{-E/RT_m} f(\alpha_m)$ is equal to zero; or that $[E/RT_m^2 + df(\alpha)/d\alpha|_{\alpha_m} A/\beta e^{-E/RT_m}]$ is zero at the maximum reaction rate. The first possibility can immediately be rejected since that would mean, $d\alpha/dT|_{T_m} = 0$, a contradiction in terms. On considering the second possibility we have

$$\left[E/RT_m^2 + \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \frac{A}{\beta} e^{-E/RT_m} \right] = 0 \quad (7)$$

or

$$\frac{E}{RT_m^2} = - \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \frac{A}{\beta} e^{-E/RT_m}$$

which, after some rearrangements could be written as

$$\frac{\beta}{RT_m^2} = \frac{AR}{E} e^{-E/RT_m} \left(- \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \right)$$

or

$$\ln \left(\frac{\beta}{T_m^2} \right) = \frac{-E}{RT_m} + \ln \left(\frac{AR}{E} \right) + \ln \left(- \left. \frac{df(\alpha)}{d\alpha} \right|_{\alpha_m} \right)$$

TABLE 1

1/g(α) and -df(α)/d α values calculated for given α

1/g(α)	-df(α)/d α		$\alpha = 0.3$		$\alpha = 0.4$		$\alpha = 0.5$		$\alpha = 0.6$		$\alpha = 0.7$	
	a	b	a	b	a	b	a	b	a	b	a	b
$1/\alpha^2$	11.111	5.555	6.250	3.125	4.000	2.000	2.778	1.389	2.041	1.021		
$1/\alpha^{1/2}$	1.826	-1.826	1.581	-1.581	1.414	-1.414	1.291	-1.291	1.195	-1.195		
$1/\alpha^{2/3}$	1.494	-2.988	1.357	-2.714	1.260	-2.520	1.186	-2.372	1.126	-2.390		
$1/\alpha^{1/4}$	1.351	-4.054	1.257	-3.772	1.189	-3.568	1.136	-3.409	1.093	-3.280		
$1/1-(1-\alpha)^{2/3}$	4.725	0.634	3.465	0.703	2.702	0.794	2.188	0.921	1.812	1.116		
$1/1-(1-\alpha)^{1/2}$	6.122	1.195	3.465	1.406	3.414	1.414	2.721	1.581	2.211	1.826		
$1/1-(1-\alpha)^{1/3}$	8.922	2.252	6.388	2.371	4.848	2.520	3.800	2.714	3.025	2.987		
$1/-\ln(1-\alpha)$	2.804	1.000	1.958	1.000	1.443	1.000	1.091	1.000	0.831	1.000		
$1/(1-\alpha)^{-1}-1$	2.333	1.400	1.500	1.200	1.000	1.000	0.667	0.800	0.429	0.600		
$1/[-\ln(1-\alpha)]^{1/2}$	1.674	-0.480	1.399	0.030	1.201	0.464	1.045	0.870	0.911	1.283		
$1/[-\ln(1-\alpha)]^{1/2}$												
$3[-\ln(1-\alpha)]^{2/3}$	1.410	-1.311	1.251	-0.585	1.130	0.090	1.030	0.771	0.940	1.515		
$2[-\ln(1-\alpha)]^{-1/3}$												
$1/[1-(1-\alpha)^{1/3}]^2$												
$(1-\alpha)^{-1/3}$												
$-1/2[1-$												
$(1-\alpha)^{1/3}]^{-2}$												
$e^{(1-\alpha)}$	79.583	-29.744	40.800	-12.824	23.500	-5.641	14.436	-2.061	0.153	-0.057		
$1/(1-\alpha)$	7.770	2.014	5.527	1.822	4.190	1.649	3.306	1.492	2.681	1.350		
$\times \ln(1-\alpha) + \alpha$												
$[-\ln(1-\alpha)]^{-2}$												
$(1-\alpha)^{-1}$	19.870	11.230	10.695	6.387	6.517	4.163	4.283	2.978	2.952	2.300		

a 1/g(α) values.b -df(α)/d α values.

Thus,

$$\ln\left(\frac{\beta}{T_m^2}\right) = \frac{-E}{RT_m} + \ln\left(\frac{AR}{-\left.\frac{df(\alpha)}{d\alpha}\right|_{\alpha_m}} E\right) \quad (8)$$

and the plot of $\ln(\beta/T_m^2)$ vs. $1/T_m$ will give a value for E from the slope.

It is interesting to note that the above relationship has some resemblance with the one put forward by Ozawa [1,2] which was obtained through entirely different considerations. Equation (8) implies that for an isokinetic process, i.e., a given $f(\alpha)$, if the T_m for a set of β occurs at a constant α_c value (within the experimental error), the $-df(\alpha)/d\alpha$ at T_m will similarly be sensibly constant. Also, it is clear that $-df(\alpha)/d\alpha$ must be positive for the same value of α if a maximum rate is to be observed. Table 1 gives an account of those commonly used kinetic expressions which can yield a maximum for the rate of reaction.

From the intercept of a plot of $\ln(\beta/T_m^2)$ vs. $1/T_m$, however, it is possible to calculate the value of the A factor once the functional form of α (i.e., $f(\alpha)$ or $g(\alpha)$) is identified. It is readily seen from Table 1 that some of the expressions cannot yield a maximum and hence should be rejected as possible choices. Others however, e.g., Avrami-Erofeev type expression with the exponent n being 2 or 3, could only yield a maximum when the occurrence of maximum rate of reaction happens at α_{\max} values higher than 0.3 and 0.4, respectively. It should be emphasised that the main interest of this study was directed to the evaluation of the most possible activation energy value from the maximum rate of reaction points and not to the elucidation of the reaction mechanism. The accurate determination of $f(\alpha)$ and/or $g(\alpha)$ requires certain assumptions pertaining to the integration of the right-hand side of eqn. (3). In a forthcoming paper, such methods are introduced to deal with identification of the reaction mechanism and hence the A factor.

REFERENCES

- 1 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
- 2 T. Ozawa, J. Therm. Anal., 7 (1975) 601.