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ON THE CALCULATION OF THE ACTIVATION ENERGY FOR SOLID STATE REACTIONS

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ABSTRACT

A novel and convenient method for the determination of the activation energy from isothermal kinetic runs has been proposed recently. A significant limitation of this method is discussed and is illustrated with an experimental example. A modification of the proposed method is suggested to circumvent this limitation.

It is generally agreed that the most reliable method for determining the activation energy in a thermal decomposition of a solid is that of observing the reaction isothermally at two or more temperatures. A novel method for calculating the activation energy from the isothermal runs has recently been proposed[1]. We wish to point out a limitation in this new method of calculation and cite a simple example to illustrate this point.

In an excellent analysis of the thermal decompositions of solids based on the theory of nucleation and nucleus growth, a generalized rate expression for a given temperature has been proposed by Ng, viz.

$$\frac{d\alpha}{dt} = \bar{k}\alpha^{1-p}(1-\alpha)^{1-q} \tag{1}$$

where α, t, and $\bar{k}$ are, respectively, the fractional decomposition, time and rate constant, while p and q are parameters lying between zero and unity inclusively for a given reaction.

Equation (1) may be rewritten as

$$\frac{d\alpha}{dt} = \bar{k}G(\alpha; p, q) \tag{2}$$

so that upon integration

$$H(\alpha; p, q) = \bar{k}t \tag{3}$$

TABLE 1

TIMES FOR THE DEHYDRATION OF $CaC_2O_4 \cdot H_2O$ AT VARIOUS VALUES OF α FOR TEMPERATURES OF 120°, 150° AND 170°C

α	t (min)		
	$T = 120°C$	$T = 150°C$	$T = 170°C$
0.1	1.53	0.74	0.55
0.2	3.50	1.20	0.71
0.3	5.52	1.61	0.88
0.4	7.51	2.08	1.07
0.5	9.51	2.55	1.25
0.6	11.61	3.08	1.44
0.7	13.91	3.62	1.63
0.8	16.31	4.21	1.84
0.9	18.90	4.87	2.12

Consider the case where the integrated equation for $H(\alpha; p, q)$ is unknown. It has been suggested[1] that for any particular fractional decomposition α_n and the corresponding time, t_n

$$H(\alpha_n; p, q) = \bar{k}t_n \tag{4}$$

so that if t'_n is the time for α_n at some other temperature, then

$$H(\alpha_n; p, q) = k't'_n \tag{5}$$

or

$$\bar{k}t_n = k't'_n = \text{constant} \tag{6}$$

Since $\bar{k}$ is inversely proportional to t_n, it has been suggested that a plot of log t_n versus $1/T$ would thus lead to a slope of $E_a/2.303R$ where E_a and R are the activation energy and gas constant, respectively.

Though eqn. (6) is mathematically correct, the use of the equation in the case of the thermal decomposition of solids may incur a sizeable error due to the time involved in achieving the desired temperatures. The lag-time or warm-up time is a congenital problem of isothermal kinetics of solid state reactions.

Consider the following experimental data in the isothermal dehydration of $CaC_2O_4 \cdot H_2O$ powder as an example using the Perkin-Elmer TGS-1 thermogravimetric instrument. The values for t, and corresponding α for 120, 150 and 170°C, are given in Table 1, the temperatures being achieved as rapidly as possible (ballistically) using five milligram samples in every case. The experiments were carried out under dry nitrogen at a flow rate of 25 ml/min.

Figure 1 shows plots of log t_n versus $1/T$ for $\alpha_n = 0.2$, 0.4, 0.6 and 0.8. The resulting values for E_a are 11.1, 13.6, 14.5 and 15.1 kcal/mol, respectively. We attribute this to the experimental lag-time which has increasing effect with reaction temperature, thus resulting in a decrease of the slope of the line for each of the plots in Fig. 1.

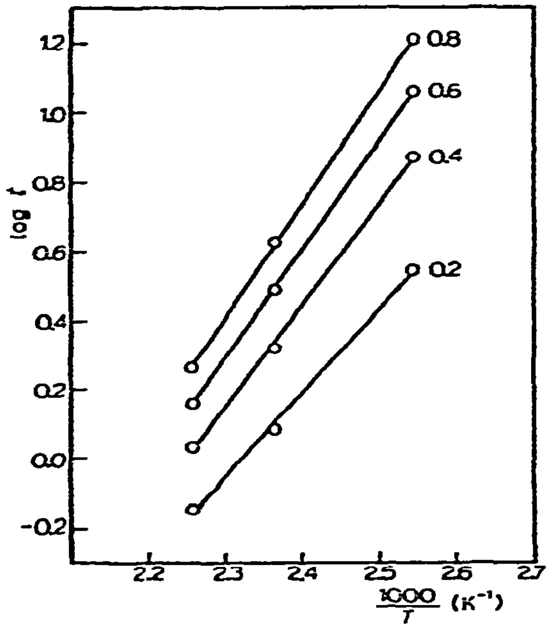

Fig. 1. Plot of log t_α as a function of the reciprocal absolute temperature for the dehydration of $CaC_2O_4 \cdot H_2O$ carried out isothermally at 120, 150, and 170°C for α_n = 0.2, 0.4, 0.6 and 0.8.

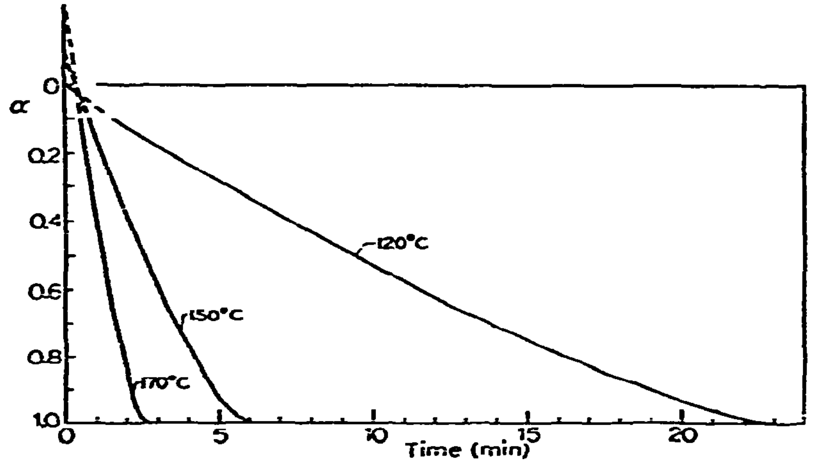

Fig. 2. Curves for the isothermal dehydration of $CaC_2O_4 \cdot H_2O$ powder under dry nitrogen at a flow rate of 25 ml/min, carried out at 120, 150 and 170°C. Extrapolation to zero time is to show effect and relative magnitude of the lag-time 170° > 150° ≫ 120°C.

The lag-time effect can be seen more clearly in Fig. 2 where the conversion curves are extrapolated to zero time.

To avoid the error of the lag-time, we suggest using the *rates* at fixed values of α. Consider eqns. (1) and (2) at any fixed value of α. Then

$$\left(\frac{d\alpha_n}{dt}\right)_{T_1} \frac{1}{k_{T_1}} = \left(\frac{d\alpha_n}{dt}\right)_{T_2} \frac{1}{k_{T_2}} \tag{7}$$

or

$$\left(\frac{d\alpha_n}{dt}\right)_{T_i} \frac{1}{k_{T_i}} = \text{constant} \tag{8}$$

Thus the same data* at $\alpha = 0.2, 0.4, 0.6$ and 0.8 yield the values $E_a = 16.6, 17.9, 17.2$ and 15.9 kcal/mol, respectively, or an average of 16.9 kcal/mol. This value may be compared with (a) the results of Dollimore et al.[2] estimated as 16.4 kcal/mol obtained isothermally** and (b) the thermodynamic value[3] for $\Delta H^\circ = 17.4$ kcal/mol. Clearly, as the lag-time approaches zero or as the lag-time becomes very much less than the half-life of the reaction, eqn. (6) of Ng should be found valid and convenient. Obviously, the time constant of the instrument plays an important role in Ng's method.

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* We have used the unsmoothed data i.e., $\Delta\alpha/\Delta t$, instead of $d\alpha/dt$ since α happens to be almost linear with t.

** Estimated from graphical data of Dollimore et al.[2].