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Note

NON-ISOTHERMAL ISOKINETIC DECOMPOSITION OF SODIUM CARBONATE

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Following our investigations concerning isokinetic conditions in non-isothermal heterogeneous solid–gas decompositions [1,2], this note deals with a natural way of obtaining such conditions. Such an isokinetic occurrence was shown by recording the thermal curves of sodium carbonate decompositions, with the heating rate $\beta = 6.7$ K min^{-1} in a derivatograph. As can be seen from Fig. 1, a sample of 0.1 g undergoes decomposition between 1143 and 1313 K after melting, with a constant rate (DTG curve) for $0.14 < \alpha < 0.84$.

The linear dependence $\alpha(T)$, which is equivalent to a linear dependence $\alpha(t)$, is shown in Fig. 2.

This isokinetic regime was not observed with other heating rates. To account for the constant rate of decomposition in the general rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{1}$$

the following conversion function was chosen

$$f(\alpha) = e^{C/T_0 + K\alpha} \tag{2}$$

where C and K are constants and T_0 is the initial temperature of decomposition (for $\alpha = 0$).

From eqns. (1) and (2), taking into account $T = T_0 + \Delta T$, eqn. (3) is obtained

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/R(T_0 + \Delta T)} \cdot e^{C/T_0 + K\alpha} \tag{3}$$

For $\Delta T < T_0$, a condition which is generally fulfilled, relationship (2) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT_0(1 - \Delta T/T_0)} \cdot e^{C/T_0(1 - K\alpha/T_0)} \tag{4}$$

or

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT_0}\, e^{C/T_0}\, e^{E\Delta T/RT_0^2}\, e^{-(CK/T_0^2)\alpha} \tag{5}$$

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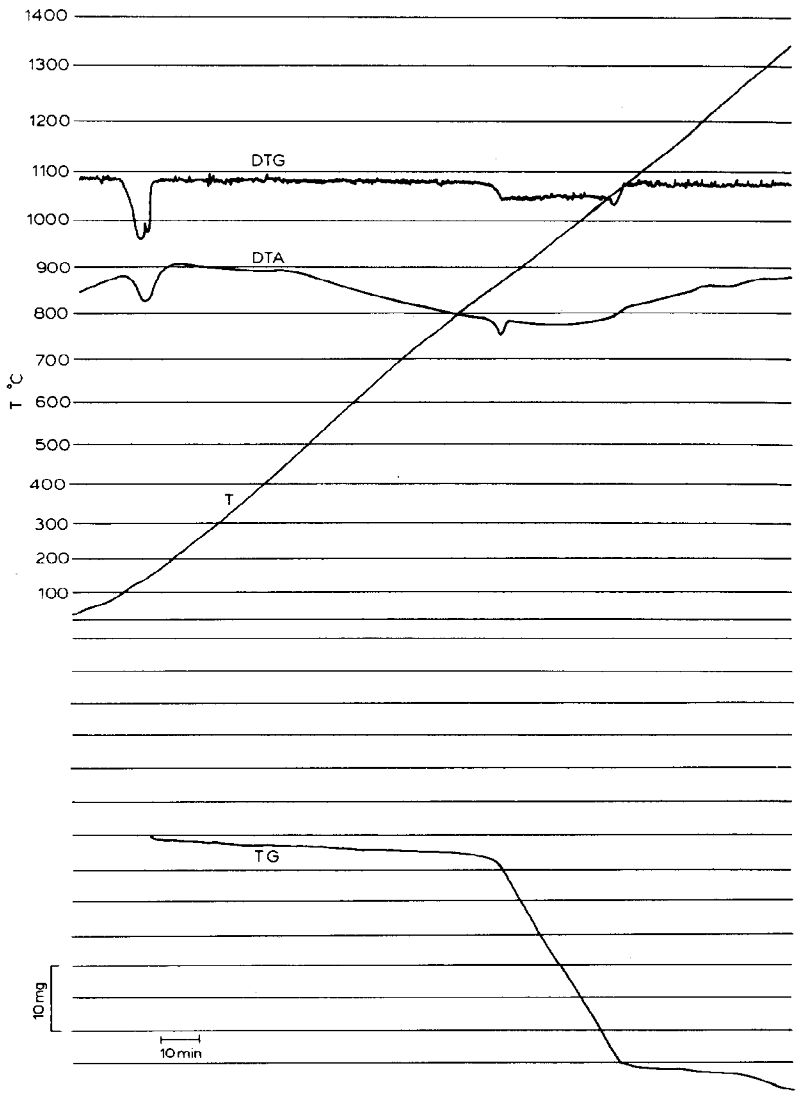

Fig. 1. The derivatogram of Na_2CO_3.

As $d\alpha/dT$ is constant in time, $d^2\alpha/dTdt = 0$.

From eqn. (5) and this last condition, eqn. (6) follows

$$\frac{E}{R}\beta = D\frac{d\alpha}{dt} \tag{6}$$

where $D = CK$ and

$$E = \frac{RD}{\beta}\frac{d\alpha}{dt} \tag{7}$$

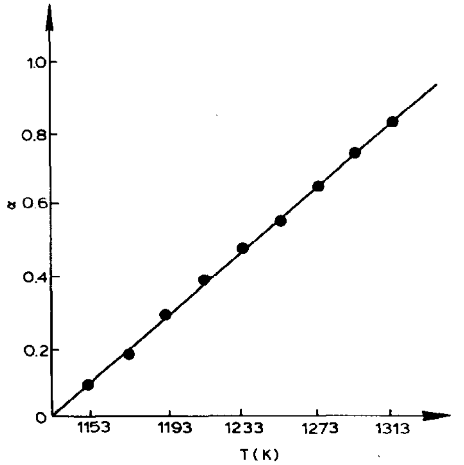

Fig. 2. The α vs. t straight line.

As the constant D cannot be evaluated from an independent experiment, eqn. (7) is not suitable for calculating the activation energy.

Equation (7) is better used to evaluate the constant D for known activation energy. In our case, using the Flynn–Wall–Ozawa method [3,4], the value $E = 36.4$ kcal mol^{-1} was obtained. From the slope of the straight line $\alpha(t)$, $d\alpha/dt = 4.5 \times 10^{-4}$ s^{-1}. Taking into account these results and using eqn. (7), the value $D = 4.5 \times 10^{6}$ K^{2} was obtained.

A task for our future research is to look for the meaning of the conversion function given by eqn. (2).

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