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Note

HEATING PROGRAM FOR A LINEAR CONVERSION–TEMPERATURE DEPENDENCE

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Using the fundamental equation of non-isothermal kinetics [1,2]

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

where in the general case [3]

$$f(\alpha)=(1-x)^{n}\alpha^{m}[-\ln(1-\alpha)]^{p} \tag{2}$$

one has to find the heating program corresponding to a given

$$\alpha=g(T) \tag{3}$$

dependence. From eqn. (3) one obtains

$$\frac{d\alpha}{dT}=g'(T) \tag{4}$$

Taking into account relationships (1) and (4), it turns out that

$$g'(T)=\frac{A}{\beta(T)}f[g(T)]\ e^{-E/RT} \tag{5}$$

or

$$\beta(T)=A\frac{f[g(T)]}{g'(T)}\ e^{-E/RT} \tag{6}$$

This is the equation needed for the program which fulfils condition (3). For the "reaction order model", i.e., $f(\alpha)=(1-\alpha)^{n}$ and

$$\alpha=a+bT \tag{7}$$

where a and b are real constants, relationship (6) takes the particular form

$$\beta(T)=\frac{A}{b}(1-a-bT)^{n}\ e^{-E/RT} \tag{8}$$

Equation (8) will be applied for a known test reaction in non-isothermal kinetics, namely, the dehydration of calcium oxalate whose kinetic parame-

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TABLE 1

Values of $\beta(T)$ for various temperatures, $T \in [485-525]$, and conversion degrees, $\alpha \in [0.2-0.8]$

T (K)	485	490	495	500	505	510	515	520	525
α	0.200	0.275	0.350	0.425	0.500	0.575	0.650	0.725	0.800
$\beta(T)$ (K min^{-1})	6.55	7.56	8.59	9.58	10.50	11.18	11.57	11.21	10.31

ters have been taken from ref. 4. A linear dependence, $\alpha(T)$, will be considered for $\alpha \in [0.2-0.8]$ and $T \in [485-525]$, i.e.

$$\begin{aligned} \alpha_1 &= 0.2 = a + 485b \\ \alpha_2 &= 0.8 = a + 525b \end{aligned} \qquad (9)$$

By solving system (9), one obtains $a = -7.075$ and $b = 0.015$. The values of the dehydration kinetic parameters are: $n = 0.98$; $A = 3.45 \times 10^7\ s^{-1} = 2.07 \times 10^9\ min^{-1}$; $E = 22700$ cal mol^{-1}. Equation (8), with these particular values of the constants and kinetic parameters, takes the form

$$\beta(T) = 1.38 \times 10^{11}(8.025\text{–}0.015T)^{0.98}\ e^{-22700/1.987T} \qquad (10)$$

Some values of the function β(T) for various temperatures and conversion degree values in the above mentioned intervals are given in Table 1.

Graphically, the plot of β vs. T is shown in Fig. 1.

CONCLUSIONS

(1) A general equation for a heating program corresponding to a given dependence, $\alpha = g(T)$, was developed.

(2) The particular form of this program with $g(T) = a + bT$ was established for the dehydration of calcium oxalate.

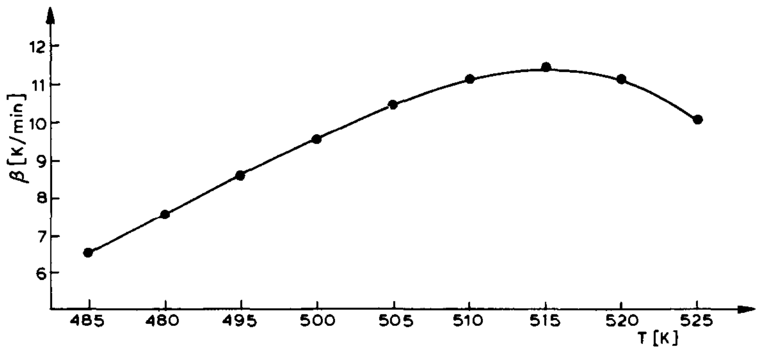

Fig. 1. The dependence of β on T.

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