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Note

NON-ISOTHERMAL KINETICS WITH NON-LINEAR TEMPERATURE PROGRAMME. IV

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The present paper aims to present two equations which allow the kinetic parameters to be obtained from α and T measurements. The equations have been tested for the dehydration of $Ca(COO)_2 \cdot H_2O$ data and the results are in good agreement with those reported in the literature [1].

In a previous paper [2] the general equation

$$t = a_1\left(\Delta T + \frac{E}{R}\, ln \frac{T}{T_0}\right) + \sum_{i \neq 1}^{z} a_i T^{i-1}\left(\frac{E}{R}\,\frac{1}{i-1} + \Delta T\right) \tag{1}$$

was established for non-linear temperature programmes where $\Delta t = t - t_0$, time difference between two successive measurements, $\Delta T = T - T_0$, the corresponding temperature difference, E is the activation energy, $R = 1.987$ cal mole^{-1} K^{-1} and a_i are the constant coefficients which allow the equation of heterogeneous processes to be written in the form

$$\begin{aligned} A\sum_{i}^{z} a_i T^i \exp(-E/RT) &= \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad \text{for } n \neq 1 \\ A\sum_{i}^{z} a_i T^i \exp(-E/RT) &= -\ln(1-\alpha) \qquad \text{for } n = 1 \end{aligned} \tag{2}$$

where α is the degree of conversion, n the reaction order and A the pre exponential factor.

Considering the high probability that

$$E/R \gg T \tag{3}$$

and writing

$$\ln T/T_0 = \ln\left(1 + \frac{\Delta T}{T_0}\right) \simeq \frac{\Delta T}{T_0} \tag{4}$$

which is true for $\Delta T/T_0 < 0.045$ (i.e. the difference of two successive temperature measurements is smaller than 10 K) eqn. (1) becomes

$$\Delta t = \frac{E}{R}\left(a_1\frac{\Delta T}{T_0} + a_i\frac{\Delta T^{i-1}}{i-1}\right) \tag{1'}$$

An estimative evaluation of the order of magnitude of a_0, a_1, a_2, shows that only a_1 has a reasonable value (about 10^{-1}), the other coefficients being negligible. Taking into account these results, the final form for the non-linear temperature programme equation is

$$\Delta t = \frac{E}{R}a_1\frac{\Delta T}{T_0} \tag{1''}$$

Equation (1″) would seem to offer the value of E from the $T(t)$ graph but, in fact, the smallest errors in the time or temperature measurements lead to large differences in the activation energy values, so the equation is not useful.

Taking into account this equation, eqn. (2) becomes

$$\left.\begin{aligned} Aa_1T\exp(-E/RT) &= \frac{1-(1-\alpha)^{1-n}}{1-n} && \text{for } n \neq 1 \\ Aa_1T\exp(-E/RT) &= -\ln(1-\alpha) && \text{for } n = 1 \end{aligned}\right\} \tag{2'}$$

which can be rearranged as follows to get the activation energy

$$\left.\begin{aligned} \frac{E}{R} &= \frac{T_0T}{T_0-T}\left[\ln\frac{T}{T_0} + \ln\frac{1-(1-\alpha_0)^{1-n}}{1-(1-\alpha)^{1-n}}\right] && \text{for } n \neq 1 \\ \frac{E}{R} &= \frac{T_0T}{T_0-T}\left[\ln\frac{T}{T_0} + \ln\frac{\ln(1-\alpha_0)}{\ln(1-\alpha)}\right] && \text{for } n = 1 \end{aligned}\right\} \tag{2''}$$

TABLE 1

Values of K for $n=1$–3

α	K		
	$n=1$ [a]	$n=2$	$n=3$
0.30	−1.030930	−0.847298	0.040005
0.35	−0.842151	−0.619039	0.312519
0.40	−0.671727	−0.405465	0.575364
0.45	−0.514437	−0.200671	0.835421
0.50	−0.366513	0.000000	1.098612
0.55	−0.225011	0.200671	1.370742
0.60	−0.087422	0.405465	1.658228
0.65	0.048621	0.619039	1.968966
0.70	0.185627	0.847298	2.313635

[a] For $n=1$, $K=\ln[-\ln(1-\alpha)]$.

where T_0, T are two successive temperature measurements ($T_0 < T$) and α_0, α are the corresponding degrees of conversion.

This equation has been tested for the dehydration of $Ca(COO)_2 \cdot H_2O$ using the data table offered by Leyko et al. [3]. The data are given for three different heating rates: $\beta_1 = 2.3$ K min^{-1}, $\beta_2 = 7.4$ K min^{-1}, and $\beta_3 = 14.8$ K min^{-1}. The mean values of the kinetic parameters are $E = 23.5$ kcal mole^{-1}, $n = 0.95$ and $A = 10^8$ sec^{-1}, in good agreement with those found in the literature. Moreover, the highest accuracy was obtained using the first heating rate (the smallest one) for values of the degree of conversion submitted to the condition $0.3 < \alpha < 0.7$.

In a rough but more operational way, eqn. (2″) can be written as

$$E/R = \frac{T_0 T}{\Delta T}\left(-\frac{\Delta T}{T_0} + K - K_0\right) \qquad (2''')$$

where $K = \ln[(1-\alpha)^{1-n} - 1]$ and can be chosen from Table 1.

With this form we have analysed the same data [3] for the dehydration of calcium oxalate and the results were: (i) for β_1: $E = 24.5$ kcal mole^{-1}, $A = 10^8$ sec^{-1}; (ii) for β_2: $E = 22.8$ kcal mole^{-1}, $A = 10^8$ sec^{-1}; (iii) for β_3: $E = 21.8$ kcal mole^{-1} and the same A, very close to the already known values [1].

CONCLUSION

From the general form of the non-linear temperature programme equation, which was given in a previous paper [2], we have derived two simpler and more operational forms, eqns. (2″) and (2‴), which have been tested for the dehydration reaction of $Ca(COO)_2 \cdot H_2O$. The results are in a good agreement with those given in the literature [1].

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