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Note

FRACTION-TIME AND FRACTION-TEMPERATURE IN NONISOTHERMAL KINETICS

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This paper presents the results of an attempt to generalize the half-time method (or generally the fraction-time method) [1] from isothermal to nonisothermal kinetics. In order to do that, one has to consider Ozawa's reduced time θ defined by [2]

$$\theta = \int_0^t e^{-E/RT}\, dt \tag{1}$$

which appears in the integral kinetic equation

$$F(\alpha) = A \int_0^t e^{-E/RT}\, dt \tag{2}$$

where α is the conversion degree, A is the pre-exponential factor, E is the activation energy, t is the time, and $F(\alpha)$ is the integrated function of conversion [3].

Considering a constant heating rate, a, of the investigated chemical system ($a = dT/dt$), from eqn. (1) it follows

$$\theta = \frac{1}{a}\int_0^T e^{-E/RT}\, dT \tag{3}$$

or through integration by parts

$$\theta = \frac{E}{aR}\, p\left(\frac{E}{RT}\right) \tag{4}$$

where according to Doyle's approximation the function $p(E/RT)$ is given by [4]

$$\ln p\left(\frac{E}{RT}\right) = -5.330 - 1.0516\frac{E}{RT} \tag{5}$$

for $E/RT \geqslant 20$.

In the framework of the "reaction order" model, $F(\alpha)$ is given by

$$F(\alpha) = \frac{1}{(n-1)}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] \tag{6}$$

where n is the reaction order. From eqns. (1)–(4) and (6),

$$\frac{1}{(n-1)}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] = \frac{AE}{aR}\, p\left(\frac{E}{RT}\right) \tag{7}$$

The fraction-reduced time will now be defined as the reduced time necessary for the difference $(1-\alpha)$ to reach the fractionary value f. On the basis of eqn. (3), it is obvious that every value of the fraction-reduced time is associated with a fraction-temperature value, T_f, necessary for the same difference to reach the value f. For $f = 1/2$ and $1/4$, eqn. (7) becomes respectively

$$\frac{1}{(n-1)}(2^{n-1}-1) = \frac{AE}{aR}\, p\left(\frac{E}{RT_{1/2}}\right) \tag{8}$$

and

$$\frac{1}{(n-1)}(4^{n-1}-1) = \frac{AE}{aR}\, p\left(\frac{E}{RT_{1/4}}\right) \tag{9}$$

From eqns. (8) and (9)

$$\frac{2^{n-1}-1}{4^{n-1}-1} = \frac{p\left(\frac{E}{RT_{1/2}}\right)}{p\left(\frac{E}{RT_{1/4}}\right)} \tag{10}$$

or, taking into account Doyle's approximation, eqn. (5)

$$\frac{2^{n-1}-1}{4^{n-1}-1} = \mathrm{e}^{-1.0516E/R(1/T_{1/2}-1/T_{1/4})} \tag{11}$$

On the other hand, the reaction rates at the temperatures $T_{1/2}$ and $T_{1/4}$, $r_{1/2}$ and $r_{1/4}$, are given by

$$r_{1/2} = A\,\mathrm{e}^{-E/RT_{1/2}}(1/2)^n \tag{12}$$

$$r_{1/4} = A\,\mathrm{e}^{-E/RT_{1/4}}(1/4)^n \tag{13}$$

so that

$$\frac{r_{1/2}}{r_{1/4}} = 2^n\,\mathrm{e}^{-E/R(1/T_{1/2}-1/T_{1/4})} \tag{14}$$

Combining eqns. (11) and (14) gives

$$\frac{\ln \frac{1}{2^n}\frac{r_{1/2}}{r_{1/4}}}{\ln \frac{2^{n-1}-1}{4^{n-1}-1}} = \frac{1}{1.0516} \tag{15}$$

Using an experimental device able to record the DTG curve, the reaction rates $r_{1/2}$ and $r_{1/4}$ are easily determined. Then, using eqn. (15), the reaction order, n, can be evaluated *.

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* To solve eqn. (15), a programmable minicomputer might be used.

For $n = 1$, instead of eqns. (8) and (9) one gets

$$\frac{AE}{aR}\,\mathrm{p}\left(\frac{E}{RT_{1/2}}\right) = \ln 2 \tag{16}$$

$$\frac{AE}{aR}\,\mathrm{p}\left(\frac{E}{RT_{1/4}}\right) = \ln 4 \tag{17}$$

or, using Doyle's approximation and taking logarithms

$$1.0516\frac{E}{R}\left(\frac{1}{T_{1/2}} - \frac{1}{T_{1/4}}\right) = \ln 2 \tag{18}$$

which allows evaluation of the activation energy E.

To check the validity of this method, the dehydration of calcium oxalate was used as a test reaction. For this reaction, according to the literature data, $n \simeq 1$ and $20 < E < 24$ kcal mole^{-1} [5]. Thus, using eqn. (18) $E = 23.7$ kcal mole^{-1} was found, in satisfactory agreement with the values reported in the literature.

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