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Note

MORE ON THE TEMPERATURE INTEGRAL

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ABSTRACT

An algorithm to calculate the activation energy value from the integral equation of nonisothermal kinetics with linear heating rate is suggested.

Many papers are devoted to the temperature integral and the integral method [1]. The topics remain open to discussion since this integral cannot be solved exactly [2] and all the methods offer only approximate solutions, even when they claim to be exact [3].

Following our earlier work [4], this paper aims to establish an algorithm to compute the value of E, the activation energy, from the integral equation of nonisothermal kinetics with linear heating rate.

Consider the usual form of this integral equation

$$\int_0^{\alpha} \frac{\mathrm{d}x}{f(1-x)} = \frac{A}{a}\int_0^T \exp(-E/Ry)\,\mathrm{d}y \tag{1}$$

where the notations have their usual meanings.

For two different heating rates $a_1 > a_2$, two different temperatures, T_1 and T_2, will correspond to a given degree of conversion, α, i.e. to a given value of the conversion integral. Obviously, $T_1 > T_2$, and from eqn. (1) one obtains

$$a_2\int_0^{T_1} \exp(-E/Ry)\,\mathrm{d}y = a_1\int_0^{T_2} \exp(-E/Ry)\,\mathrm{d}y \tag{2}$$

Relationship (2) may be considered as a function of E

$$g(E) = a_2\int_0^{T_1} \exp(-E/Ry)\,\mathrm{d}y - a_1\int_0^{T_2} \exp(-E/Ry)\,\mathrm{d}y \tag{3}$$

Thus the required value of E is the solution, E_0, of the equation

$$g(E) = 0 \tag{4}$$

Let us investigate first the conditions of existence of the solutions for eqn. (4). It is easy to see that $g(E)$ is defined on R_+ and that:

$$\lim_{E \to 0} g(E) = a_2 T_1 - a_1 T_2 \tag{5}$$

$$\lim_{E \to \infty} g(E) = 0 \tag{6}$$

The first derivative of $g(E)$ may also be obtained

$$g'(E) = a_1 T_2 \exp(-E/RT_2)\left[\frac{a_2 T_1}{a_1 T_2} \exp\left(\frac{E}{R}\frac{T_1 - T_2}{T_1 T_2}\right) - 1\right] \tag{7}$$

Since

$$\exp\left(\frac{E}{R}\frac{T_1 - T_2}{T_1 T_2}\right) > 1 \tag{8}$$

we have two possibilities: $a_2 T_1/a_1 T_2$ is either greater than or less than 1.

(a) For $a_2 T_1/a_1 T_2 > 1$ (eqn. (9)), we have $g'(E) > 0$ for all values of E. This means that $g(E)$ is a monotonic function increasing from g(0) to g(∞). On the other hand, eqn. (9) leads to

$$a_2 T_1 - a_1 T_2 > 0 \tag{10}$$

which means, finally, that $g(0)$ is higher than $g(\infty)$. This contradiction leads to the conclusion that assumption (a) is invalid.

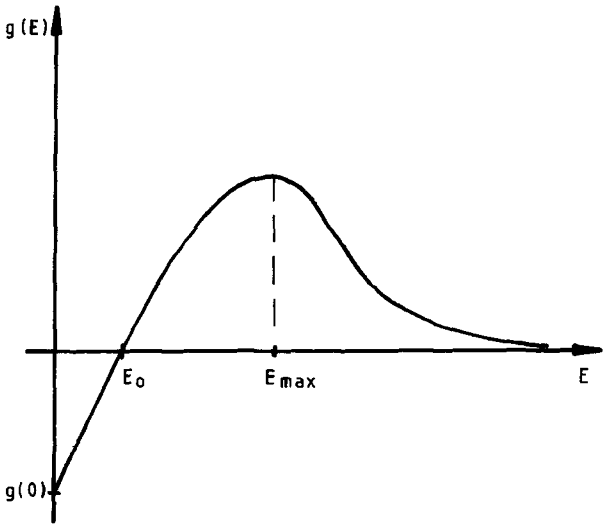

Fig. 1. Plot of g(E).

(b) For $a_2T_1/a_1T_2 < 1$ eqn. (11) and from $g'(E) = 0$ one obtains

$$E_{\text{extremum}} = R\frac{T_1T_2}{T_1 - T_2} \ln \frac{a_1T_2}{a_2T_1} \quad (12)$$

One observes that

$$g'(E < E_{\text{extremum}}) > 0 \quad (13)$$

$$g'(E > E_{\text{extremum}}) < 0 \quad (14)$$

It follows that $g(E_{\text{extremum}})$ is a maximum value of the function. Obviously $g(E_{\max}) > 0$.

Equation (11) leads to

$$a_2T_1 - a_1T_2 = g(0) < 0 \quad (15)$$

ALGORITHM

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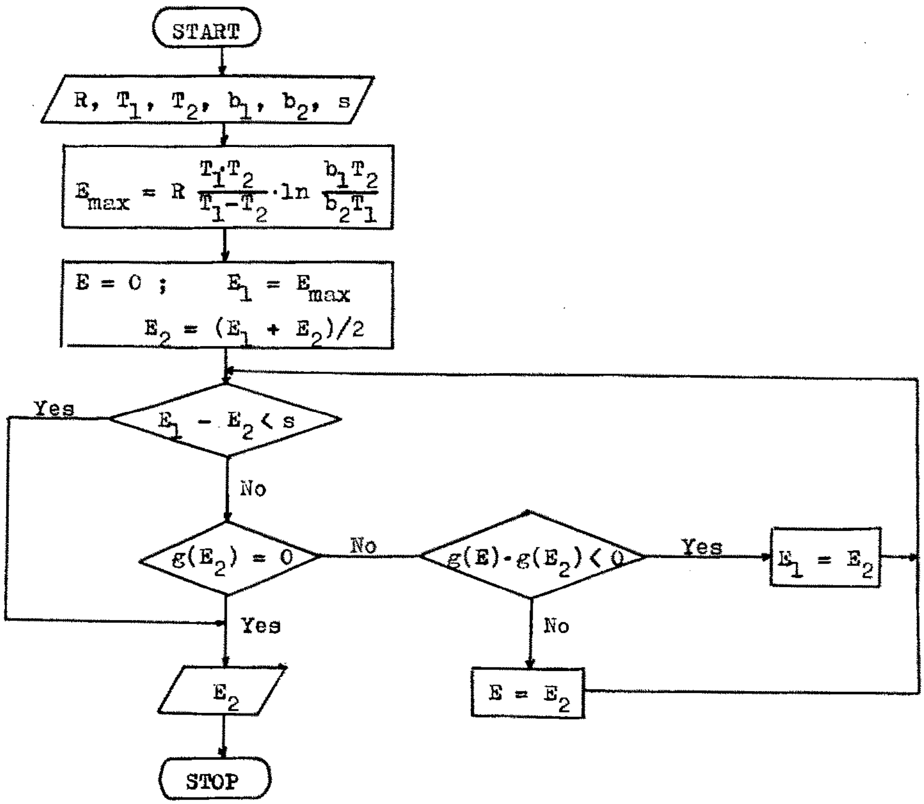

Fig. 2. Algorithm to compute the activation energy.

As a result of the above considerations a graphical representation of $g(E)$ may be obtained, as shown in Fig. 1.

The solution of eqn. (4), i.e. E_0, will then lie between 0 and E_{max}, as given by eqn. (12).

Relationship (11) may also be used as a criterion of the existence of a unique mechanism of reaction. If, for a given α, the corresponding temperatures at two different heating rates fulfill the condition (11), we may suppose that the reaction occurs according to the same mechanism irrespective of the heating programme. If condition (11) is not fulfilled, we may be certain that the mechanism, i.e. $f(1-\alpha)$, differs as the heating rates change.

An algorithm to calculate E_0 with an accuracy better than a desired value, s, is given in Fig. 2, based on the above considerations.

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