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Short Communication

LOGISTIC HEATING PROGRAM IN THERMAL ANALYSIS AND NON-ISOTHERMAL KINETICS

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Use of the logistic rule is proposed for programmed heating in thermal analysis. An algorithm is presented for solving the temperature integral of non-isothermal kinetics.

In thermoanalytical practice a sharp difference is made between the study of transformations under isothermal and non-isothermal conditions. Formally, though, the isothermal process may be considered the boundary case of the non-isothermal process with the condition $\frac{dT}{dt} \rightarrow 0$. In the general case, the technique of isothermal investigations consists of two successive stages: the non-programmed (or in some cases the linearly programmed) heating of the sample to a selected temperature, and the subsequent keeping of the sample at this temperature until the transformation is ended. The idea to replace the non-isothermal and isothermal stages by one program combined analytically is an obvious one. The logistic rule of heating appears suitable for such a program. It is expressed mathematically by the known Perl equation (1):

$$\frac{dT}{dt} = cT(T_0 - T) \tag{1a}$$

or

$$T = \frac{T_0}{1 + \lambda \exp(-cT_0 t)} \tag{1b}$$

where c and λ are constants and T_0 is the upper boundary of temperature rise. For logistic temperature programming the kinetic equation

$$\frac{d(\alpha)}{dt} = A \exp - \frac{E}{RT} f(\alpha) \tag{2}$$

can be written in the following form:

$$g(\alpha) = \int_0^\alpha \frac{d(\alpha)}{f(\alpha)} = \frac{A}{c} \int_0^T \frac{\exp\left(-\frac{E}{RT}\right)}{T(T_0 - T)} dT \tag{3}$$

(the symbols being those generally applied for non-isothermal kinetics).

The following task is to find an integration procedure for the kinetic equation (3). For this purpose, starting from the train of thought of Frank-Kamenetsky [2, 3], it is necessary to transform the expression $(T_0 - T)$ into an exponential function, that is $(T_0 - T) = a \exp \frac{b}{RT}$, or $\ln (T_0 - T) = \ln a + \frac{b}{RT}$, where a and b are constants. Utilizing the Frank-Kamenetsky transformation, the kinetic equation [3] will assume the form

$$g(\alpha) = \frac{A}{ac} \int_0^T T^{-1} \exp\left(-\frac{E+b}{RT} dT\right) \tag{4}$$

The solution of this temperature integral has already been reported in [4] for the condition $E \gg RT$; its general form is

$$\int_0^T T^z \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^{z+2}}{E + (z+2)RT} e^{-E/RT}$$

Finally, after the necessary mathematical transformations, one obtains:

$$g(\alpha) = \frac{A}{ac} \frac{RT}{(E+b) + RT} \exp\left(-\frac{E+b}{RT}\right)$$

or

$$g(\alpha) = \frac{A}{c} \frac{RT \exp\left(-\frac{E}{RT}\right)}{(T_0 - T)(E + b + RT)} \tag{5}$$

Consequently, by performing the thermoanalytical experiment according to the logistic heating program, one can determine the kinetic value of the activation energy E in the interval of the exponential rise of temperature in this program.

Besides the Perl curve, another logistic curve, that of Gompertz [1], is also known:

$$T = T_0 \exp(-\lambda e^{-ct})$$

However, its utilization for temperature programming does not provide any particular advantage, while the difficulty of solving the temperature integral increases substantially.

References

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