

EXPONENTIAL TEMPERATURE CHANGE IN THERMAL ANALYSIS AT NON-ISOTHERMAL KINETICS

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The applying of exponential temperature programming: $dT/dt = \sigma T$ or $T = T_0 e^{\sigma t}$ in thermal analysis at non-isothermal kinetics is discussed. An approach for the integration of the temperature integral is presented.

For non-isothermal kinetics [1–3], mainly two types of temperature programming are in use, namely the linear program $T = T_0 + at$ (or $dT/dt = a$), and the hyperbolic program $1/T = 1/T_0 - bt$ (or $dT/dt = bT^2$). However, an intermediate program might also be suggested in the form of $dT/dt = \sigma T$ (or $T = T_0 e^{\sigma t}$). It should be noted here that the spontaneous cooling of a body to ambient temperature takes place according to Newton's well-known exponential relationship. Expressing the differential kinetic equation $d\alpha/dt = k(T)f(\alpha)$ relative to α and T yields

$$\frac{d\alpha}{dT} = \frac{A}{\sigma T} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

or

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = F(\alpha) = \frac{A}{\sigma} \int_{T_0}^T \frac{\exp\left(-\frac{E}{RT}\right)}{T} dT \quad (2)$$

(the symbols used are the generally accepted ones). To render the solution of the temperature integral more convenient, let us write Eq. (2) in the following form:

$$F(\alpha) = \frac{A}{\sigma} \int_0^T \frac{\exp\left(-\frac{E}{RT}\right)}{T} dT - \frac{A}{\sigma} \int_0^{T_0} \frac{\exp\left(-\frac{E}{RT}\right)}{T} dT \quad (3)$$

Let us assume that the temperature integral derived from the non-isothermal experiment satisfies the condition $T \gg T_0$. Then Eq. (3) can be written in the following simple form [4]:

$$F(\alpha) = \frac{A}{\sigma} \int_0^T \frac{\exp\left(-\frac{E}{RT}\right)}{T} dT = \frac{ART}{\sigma(E+RT)} \exp\left(-\frac{E}{RT}\right) \quad (4)$$

Let us introduce a new variable $x = -\frac{E}{RT}$.

Then

$$dT = \frac{RT^2}{E} dx$$

Substituting this relationship into Eq. (4) yields:

$$F(\alpha) = \frac{A}{\sigma} \int_x^{-\infty} \frac{\exp\left(-\frac{E}{RT}\right)}{x} dx \quad (5)$$

Finally a tabular integral is obtained which cannot be integrated elementarily [5]:

$$\int \frac{e^x}{x} dx = \ln x + x + \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3!} + \dots \quad (6)$$

In order to overcome this basic difficulty, we suggest the third method for solving the temperature integral. Let us assume that a solution exists having the form

$$\int_0^T \frac{\exp\left(-\frac{E}{RT}\right)}{T} dT = \frac{RT^\gamma}{E} \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Differentiation of the right-hand side of this equation under the condition that $\gamma = \text{const.}$ will yield, after some simple transformations,

$$\gamma \frac{RT^\gamma}{E} = 1 - T^{\gamma-1} \quad (8)$$

Within a temperature range between T_1 and T_2 , some mean value $\bar{\gamma}$ can be determined:

$$\frac{T_1^{\bar{\gamma}}}{T_2^{\bar{\gamma}}} = \frac{1 - T_1^{\bar{\gamma}-1}}{1 - T_2^{\bar{\gamma}-1}} \quad (9)$$

The solution of this transcendent equation relative to $\bar{\gamma}$ can readily be obtained by computer or graphically, by plotting the relationships

$$z \text{ vs. } \frac{T_1^{\bar{\gamma}}}{T_2^{\bar{\gamma}}} \text{ and } z \text{ vs. } \frac{1 - T_1^{\bar{\gamma}-1}}{1 - T_2^{\bar{\gamma}-1}}$$

The intersection of the two curves will yield the mean value $\bar{\gamma} = \phi \approx 1$.

In this way, we finally arrive to

$$F(\alpha) = \frac{A}{\sigma} \cdot \frac{RT^\phi}{E} \exp\left(-\frac{E}{RT}\right) \quad (10)$$

The activation energy E of the transformation process can then be determined by plotting

$$\ln \frac{F(\alpha)}{T} = -\frac{E}{RT} + \ln \frac{AR}{\sigma(E + RT)} \quad \text{or} \quad \ln \frac{F(\alpha)}{T^\phi} = -\frac{E}{RT} + \ln \frac{AR}{\sigma E} \quad (11)$$

for the chosen temperature range T_1 to T_2 .

Finally, let us consider what has been said for the function $f(\alpha) = (1 - \alpha)^n$. This will yield

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ART^\phi}{\sigma E} \exp\left(-\frac{E}{RT}\right) \quad (12)$$

Conforming to the train of ideas in [6], the pre-exponential factor in the Arrhenius equation is

$$A = \frac{(1 - \alpha_s)^{1-n}}{n} \cdot \frac{\sigma E}{RT_s} \exp\left(+\frac{E}{RT_s}\right) \quad (13)$$

Substitution of Eq. (13) into Eq. (12) will afford the full expression in the following form:

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{(1 - \alpha_s)^{1-n}}{n} \left(\frac{T^\phi}{T_s}\right) \exp\left(\frac{E}{RT_s}\right) \exp\left(-\frac{E}{RT}\right) \quad (14)$$

and for the point (α_s, T_s) :

$$\frac{1 - (1 - \alpha_s)^{1-n}}{1 - n} = \frac{(1 - \alpha_s)^{1-n}}{n} \cdot \left(\frac{T_s^\phi}{T_s}\right) \quad (15)$$

From Eq. (15), if the value of ϕ has previously been established, the relationship between α_s and n can readily be derived:

$$1 - \alpha_s = \frac{n^{\frac{1}{1-n}}}{[n + (1 - n)T_s^{\phi-1}]^{\frac{1}{1-n}}} \approx n^{\frac{1}{1-n}} \quad (16)$$

Since the mathematical difficulties resulting from exponential temperature change programs can be overcome in the presented way, it may be presumed that this type of temperature programming will widely be utilized in the practice and theory of thermal analysis.

References

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