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Note

SOME APPROXIMATIONS OF THE TEMPERATURE INTEGRAL THROUGH INTEGRATION OVER SMALL TEMPERATURE INTERVALS

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Following our research concerning the problems of non-isothermal kinetic analysis using integration over small temperature intervals [1–3], this paper deals with the same approximations of the temperature integral. Such approximations allow:

(a) the value of the temperature integral to be computed with a known value of the activation energy;

(b) an expression to be obtained for calculating the activation energy, if its value is unknown. If more complicated expressions can be used for the temperature integral, case (b) needs simple expressions, to facilitate the calculations.

To simplify the calculations, one assumes that for $T \in [T_1, T_2]$ with $\Delta T = T_2 - T_1 \leqslant 20$ K, the functions depending on temperature mainly $e^{-E/RT}$, can be considered as linear.

Considering the fundamental equation of non-isothermal kinetics [4,5]

$$\frac{d\alpha}{dT} = \frac{A_r}{\beta} T^r f(\alpha)\, e^{-E/RT} \tag{1}$$

through the separation of variables and integration, we obtain

$$\int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{f(\alpha)} = \frac{A_r}{\beta} \int_{T_1}^{T_2} T^r\, e^{-E/RT} \tag{2}$$

The integral $\int_{T_1}^{T_2} T^r\, e^{-E/RT} dT$ will be called the temperature integral over small temperature intervals. For $r = 0$, it takes the simple form $\int_{T_2}^{T_2} e^{-E/RT} dT$. Some approximations of these integrals are given below.

APPROXIMATION 1

From mathematical analysis it is known that if a function $f(x)$ is continuous in the closed interval $[a, b]$, then [6]

$$\int_a^b f(x)\, dx = (b - a)\, f(\xi) \tag{3}$$

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with $\xi \in (a, b)$. If $f(x)$ is a linear function, i.e.

$$f(x) = mx + n \tag{4}$$

then

$$\xi = \frac{a+b}{2} \tag{5}$$

Taking into account relationships (3)–(5), the temperature integrals over small temperature intervals take the following forms [1]

$$\int_{T_1}^{T_2} T^r \,\mathrm{e}^{-E/RT} \mathrm{d}T \approx (T_2 - T_1) T_{12}^r \,\mathrm{e}^{-E/RT_{12}} \tag{6}$$

$$\int_{T_1}^{T_2} \mathrm{e}^{-E/RT} \mathrm{d}T \approx (T_2 - T_1)\, \mathrm{e}^{-E/RT_{12}} \tag{7}$$

with

$$T_{12} = \frac{T_1 + T_2}{2} \tag{8}$$

APPROXIMATION 2

The following theorem from mathematical analysis will be used: if the functions $f(x)$ and $g(x)$ are continuous in the closed interval $[a, b]$ and $g(x)$ does not change its sign in the same interval, there is a point $\xi \in (a, b)$ such that

$$\int_a^b f(x)\, g(x)\, \mathrm{d}x = f(\xi) \int_a^b g(x)\, \mathrm{d}x \tag{9}$$

In terms of eqn. (9), the temperature integral over small temperature intervals can be calculated as follows

$$\int_{T_1}^{T_2} T^r \,\mathrm{e}^{-E/RT} T = \int_{T_1}^{T_2} T^{r+2} \,\mathrm{e}^{-E/RT} \frac{\mathrm{d}\,T}{T^2} \approx T_{12}^{r+2} \frac{R}{E} \left[\mathrm{e}^{-E/RT_2} - \mathrm{e}^{-E/RT_1}\right] \tag{10}$$

with T_{12} given by eqn (8). This approximation is better than the first one as T_{12}^{r+2} (T_{12} being the source of errors) enters only as a factor and does not enter into the exponential.

APPROXIMATION 3

Using the trapezoidal method [7] for $n = 1$ we obtain

$$\int_{T_1}^{T_2} T^r \,\mathrm{e}^{-E/RT} \mathrm{d}T \approx \frac{T_2 - T_1}{2} \left[T_2^r \,\mathrm{e}^{-E/RT_2} + T_1^r \,\mathrm{e}^{-E/RT_1}\right] \tag{11}$$

$$\int_{T_1}^{T_2} \mathrm{e}^{-E/RT} \mathrm{d}T \approx \frac{T_2 - T_1}{2} \left[\mathrm{e}^{-E/RT_2} + \mathrm{e}^{-E/RT_1}\right] \tag{12}$$

APPROXIMATION 4

Using Simpson's formula [8] for $n = 2$ it turns out that

$$\int_{T_1}^{T_2} T^r \mathrm{e}^{-E/RT} \approx \frac{T_2 - T_1}{6} \left[T_2^r \mathrm{e}^{-E/RT_2} + 4T_{12}^r \mathrm{e}^{-E/RT_{12}} + T_1^r \mathrm{e}^{-E/RT_1} \right] \tag{13}$$

where T_{12} is given by eqn. (8). The error corresponding to Simpson's method is given by [8]

$$R = -\frac{h^5}{90} \mathrm{f}^{\mathrm{IV}}(\xi) \tag{14}$$

with

$$\xi \in [T_{12} - h, T_{12} + h]$$

and

$$h = \frac{T_2 - T_1}{2} \tag{15}$$

For the functions whose fourth derivative vanishes, the error equals 0. Thus, taking into account that our functions $T^r \mathrm{e}^{-E/RT}$ and $\mathrm{e}^{-E/RT}$ can be approximately treated as linear, their fourth derivatives are close to zero, and the last approximation can be considered as the best one.

Taking into account the complexity of the derived expressions one can state that approximation 4 is suitable in case (a) for known activation energy whereas approximations 1–3, mainly 1, are suitable for calculating the activation energy.

For the particular case characterized by $r = 0$; $E = 22000$ cal mol^{-1}; $T_1 = 500$ K; $T_2 = 516$ K, taking $R = 1.987$ cal mol^{-1} K^{-1}, one obtains the following results.

Approximation 1

$$\int_{500}^{516} \mathrm{e}^{-22000/RT} \mathrm{d}T \approx 5.477 \times 10^{-9}$$

Approximation 2

$$\int_{500}^{516} \mathrm{e}^{-22000/RT} \mathrm{d}T \approx 5.557 \times 10^{-9}$$

Approximation 3

$$\int_{500}^{516} \mathrm{e}^{-22000/RT} \mathrm{d}T \approx 5.77 \times 10^{-9}$$

Approximation 4

$$\int_{500}^{516} e^{-22000/RT}\,\mathrm{d}T \approx 5.576 \times 10^{-9}$$

Thus, if approximation 4, as shown before, is the best one, approximation 2 leads to an error of −0.34% with respect to approximation 4, followed by approximation 1 with an error of −1.8% and approximation 3 with an error of +3.4%. Taking into account these small errors, one can conclude that all the last three approximations can be used in order to evaluate the temperature integral over small temperature intervals.

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