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EMPIRICAL FORMULA FOR THE EXPONENTIAL INTEGRAL IN NON-ISOTHERMAL KINETICS

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The exponential integral $p(x) = -\int\limits_{\infty}^{x} \frac{e^{-u}}{u^2} \cdot du$ can be approximated by means of the empirical formula $p(x) \approx \frac{e^{-x}}{(x-d)(x+2)}$ with $d = \frac{16}{(x^2 - 4x + 84)}$. If $x > 1.6$, errors are less than 0.5%.

The rate of a simple homogeneous reaction is given by the following formula

$$-\frac{dc}{dt} = kf(c) \tag{1}$$

where c stands for the concentration, t for time, k is the rate constant and $f(c)$ is a certain function of the concentration. The rate constant obeys the Arrhenius equation and if the kinetic run is performed under non-isothermal conditions characterized by a certain temperature programme $T = \phi(t)$, the following differential equation is valid [1]:

$$-\frac{dc}{f(c)} = Ze^{-E/RT} \psi \cdot (T)dT \tag{2}$$

where Z stands for the pre-exponential factor in the Arrhenius equation, E for the activation energy, and $\psi(T)$ is the inverse function of $\phi(t)$, i.e. $\psi \cdot (T)dt = dt$.

In the case of heterogeneous non-isothermal reactions a formal approach is frequently used, by considering an analogous differential equation to be valid [2], viz.:

$$\frac{d\alpha}{f(\alpha)} = Ze^{-E/RT} \psi \cdot (T)dt \tag{3}$$

where α stands for the transformation degree (conversion) of the reactant.

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If the heating programme performs a linear variation of $1/T$

$$\frac{1}{T} = a - qt \tag{4}$$

equations (2) and (3) become

$$-\frac{dc}{f(c)} = -\frac{Z}{q} e^{-E/RT} d(1/T) \quad \text{and} \quad \frac{d\alpha}{f(\alpha)} = -\frac{Z}{q} e^{-E/RT} d(1/T) \tag{5}$$

The right-hand terms of these equations can be integrated [3]:

$$g(c) = \frac{ZR}{qE} e^{-E/RT} \quad \text{and} \quad g(\alpha) = \frac{ZR}{qE} e^{-E/RT} \tag{6}$$

where the symbols

$$g(c) = -\int_{c_0}^{c} \frac{dc}{f(c)} \quad \text{and} \quad g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} \tag{7}$$

have been used.

In the case of a linear heating programme

$$T = T_0 + qt \tag{8}$$

equations (2) and (3) become

$$-\frac{dc}{f(c)} = \frac{Z}{q} e^{-E/RT} dT \quad \text{and} \quad \frac{d\alpha}{f(\alpha)} = \frac{Z}{q} e^{-E/RT} dT \tag{9}$$

Formal integration gives

$$g(c) = \frac{Z}{q} \int_{0}^{T} e^{-E/RT} dT \quad \text{and} \quad g(\alpha) = \frac{Z}{q} \int_{0}^{T} e^{-E/RT} dT \tag{10}$$

but the exponential integral in the right-hand term cannot be obtained in finite form. This is why approximate formulae are frequently used.

One of the best approaches, used by Coats and Redfern [4], is the following

$$\int_{0}^{T} e^{-E/RT} dT \approx \left(1 - \frac{2RT}{E}\right) \frac{RT^2}{E} e^{-E/RT} \tag{1}$$

A better approach

$$\int_{0}^{T} e^{-E/RT} dT \approx \frac{RT^2}{E + 2RT} e^{-E/RT} \tag{12}$$

has recently been proposed by Gorbachev [5].

Introducing the notation $u = E/RT$, equations (10) become

$$g(c) = \frac{ZE}{Rq}\,p(x) \quad \text{and} \quad g(\alpha) = \frac{ZE}{Rq}\,p(x) \tag{13}$$

where $p(x)$ stands for the exponential integral

$$p(x) = -\int_{\infty}^{x} \frac{e^{-u}}{u^2}\,du = \int_{x}^{\infty} \frac{e^{-u}}{u^2}\,du \tag{14}$$

Since

$$\int_{0}^{T} e^{-E/RT}\,dT = \frac{E}{R}\,p(x) \tag{15}$$

the approach (11) gives

$$p(x) \approx \left(\frac{1}{x^2} - \frac{2}{x^3}\right)e^{-x} = \frac{x-2}{x^3}\,e^{-x} \tag{16}$$

In a similar way, Gorbachev's approach (12) can be written in the following form

$$p(x) \approx \frac{e^{-x}}{x(x+2)} \tag{17}$$

In order to find the region where the approaches (16) and (17) can be used, $p(x)$ values calculated by means of these formulae have been compared with the accurate $p(x)$ values [6]. The calculations have shown the error of $p(x)$ to be less than 0.5% only for $x > 36$ when formula (16) is used. Formula (17) is better, giving errors less than 0.5% if $x > 18$.

Comparison of the accurate $p(x)$ values with the values calculated by means of (17) showed the possibility of approximating $p(x)$ by means of an empirical formula of the following form

$$p(x) \approx \frac{e^{-x}}{(x-d)(x+2)} \tag{18}$$

For the empirical parameter d the following expression has been found:

$$d = \frac{16}{x^2 - 4x + 84} \tag{19}$$

Relation (18) gives $p(x)$ with an error less than 0.5%, even in the region $1.6 < x \leq 18$. It gives the same values as (17) in the region $18 < x \leq 36$. For $x > 36$ all approaches (16), (17) and (18) give practically the same $p(x)$ value.

The proposed empirical formula (18) can be used in all practical cases, since even if the activation energy is only $E = 4$ kcal/mole, (18) gives good results up to 1000°. If E is higher, formula (18) can also be used for even higher temperatures.

References

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