Letter to the Editor

INVARIANT REDUCED ACTIVATION ENERGY FOR THERMOKINETIC CURVES WITH NON-PREDETERMINED ORDER OF REACTION

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Sometimes thermokinetic curves should be analyzed, even if their effective order of reaction n has not been established either from any reaction model or from experimental data, or n could not be evaluated with sufficient accuracy. For this case in [1] it was claimed that, independent of the accuracy of the determination of the true order of reaction n_{true}, the constancy of the ratio $\left(\frac{E}{n}\right)$ is observed, i.e. $\frac{E_{\text{true}}}{n_{\text{true}}} = \frac{E_x}{n_x}$, where n_x and E_x are experimentally approximated values. However, this ratio systematically overestimates the real correlation for different situations n_x; a more correct ratio is:

$$\frac{E_{\text{true}}}{n_{\text{true}}} \cdot \frac{1}{\sqrt[n_{\text{true}}-1]{n_{\text{true}}}} = \frac{E_x}{n_x} \cdot \frac{1}{\sqrt[n_x-1]{n_x}} \equiv \frac{E_x}{n_x^{\frac{n_x}{n_x-1}}}. \tag{1}$$

This relation can be derived in quite the same way as in [1]; starting from the maximum condition $\left.\frac{d^2\alpha}{dT^2}\right|_{\overline{T}} = 0$ the rate constant becomes (dashes above symbols indicate maximum situation: $\overline{\alpha^{(n)}}$, $\overline{T^{(n)}}$, $\overline{K}$)

$$\overline{K} = \frac{(1 - \overline{\alpha^{(n)}})^{1-n}}{n} \cdot \frac{E \cdot q}{k\overline{T^{(n)2}}} \tag{2}$$

and the maximum reaction intensity

$$\overline{\frac{d\alpha}{dT}} = (1 - \overline{\alpha^{(n)}})^{n} \cdot \overline{K} = \frac{1 - \overline{\alpha^{(n)}}}{n} \cdot \frac{E \cdot q}{k\overline{T^{(n)2}}} \tag{3}$$

Only one further connection must additionally be taken into account [2, 3]

$$\overline{\alpha^{(n)}} = 1 - \sqrt[1-n]{n} \cdot (2 - \bar{\eta}). \tag{4}$$

In [1] this last dependence of $\overline{\alpha^{(n)}}$ on n has been neglected (here we will neglect only the much smaller dependencies of $\overline{T^{(n)}}$ and therefore also of $\bar{\eta}$ [4] on n).

For a number of reaction orders n often examined, the reduction factors in (1) are:

n	1/3	1/2	2/3	1	1 1/2	2	3	4
$\sqrt[n-1]{n}$	5.196	4.	3.375	e = 2.718	2.25	2.	1.732	1.587
$n^{\frac{n}{n-1}}$	1.732	2.	2.25	2.718	3.375	4.	5.196	6.350

If the shape of experimental curves $\alpha^{(n)}$ is known more precisely, especially with respect to the amount and position of $\alpha\overline{T^{(n)}}$ and the asymmetry around $\bar{T}$, then from these data n can be derived directly and should not be considered as an unknown variable.

References

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