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Note

On the estimation of reaction order from the conversion degree in thermostimulated traces

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For a reaction, characterised by a single activation energy (E), pre-exponential factor (A) and reaction order (n), which obeys the Arrhenius equation, and under the condition of a constant heating rate (a),

$$\frac{dx}{dT} = \frac{A}{a} e^{-E/RT} (1 - x)^n \tag{1}$$

it has been shown by Gyulai and Greenhow[1], that the conversion degree (x_M) corresponding to the maximum point (indicated by the subscript M) of the differential curve can be better represented in the following improved form

$$x_M = 1 - N \cdot n^{1/(1-n)} \qquad \text{with } N = 1.062 \tag{2}$$

than in the simple form

$$x_M = 1 - n^{1/(1-n)} \tag{3}$$

They deduced their conclusion from a number of theoretically calculated reaction curves for a wide range of values of the kinetic constants ($E = 10$–100 kcal mol^{-1}, $A/a = 10^8$–10^{20} K^{-1}, $n = 0.1$–3) and their re-analysis. But this reasonable correction factor can stand only for some mean or particular choice of the kinetic constants.

It is the purpose of this note to show a direct dependence of this correction factor from the kinetic constants.

Integration of the separated eqn (1) leads for $n \neq 1$ to[2]

$$\frac{1}{n-1}\left(\frac{1}{(1-x(T))^{n-1}} - 1\right) = S(T; E, A/a) \cdot \eta\left(\frac{kT}{E}\right) \tag{4}$$

where

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$$S \equiv \frac{ART^2}{aE} \cdot e^{-E/RT} \tag{5}$$

$$\eta \equiv 1 - 2y + 6y^2 - 24y^3 + 120y^4 - + \ldots;\ y \equiv \frac{kT}{E} \ll 1 \tag{6}$$

The maximum condition $d^2x/dT^2|_{T_M} = 0$ gives

$$n(1 - x_M)^{n-1} \cdot S_M = 1 \tag{7}$$

and hence combining eqns (4)* and (7)

$$x_M = 1 - \sqrt[n-1]{1 - \frac{n-1}{n}\eta_M} = 1 - n^{-1/(n-1)} \cdot \sqrt[n-1]{1 + (n-1)(1-\eta_M)} \tag{8}$$

Because practically $y < 0.1$, one may use the expansion of the $(n - 1)$-root and gets

$$N = \sqrt[n-1]{1 + (n-1)(1-\eta_M)} \cong 2 - \eta_M \tag{9}$$

This shows that the correction factor N is directly dependent of E and T_M, but through T_M also on A and a or on A/a; more qualitatively, one can get further from eqns (8), (7) and (5), neglecting all terms with y^3 and higher orders in y,

$$\frac{dx_M}{x_M} \cong \frac{2y_M^2}{\sqrt[n-1]{n} - 1}\left(\frac{dE}{E} + \frac{dA}{A} - \frac{da}{a}\right) \tag{10}$$

From this, it follows that x_M increases gradually with increasing activation energy E, increasing pre-exponential frequency factor A and when lowering the heating rate a. These facts had been mentioned empirically by Gyulai and Greenhow[1], but could not be reflected by their fixed correction factor $N = 1.062$. This concrete value of N is valid for $\eta = 0.938$ and hence for $y = 0.0341$ or $E = 29.29\ kT_M$ (ref. 3). The relative shift of x_M in dependence from E, A and a, as expressed by eqn (10), is on account of y^2 quite small, and moreover experimentally the determination of the single point x_M is qualitative only. Therefore, it is the author's opinion, that the considered correction factor N can be helpful in the distinction of kinetic order values for different models, rather than for an evaluation of numerical values with exaggerated accuracy.

REFERENCES

1 G. Gyulai and E. J. Greenhow, *Thermochim. Acta*, 6 (1973) 254.
2 M. Balarin and A. Zetzsche, *Phys. Status. Solidi*, 3 (1963) K387.
3 M. Balarin, *J. Therm. Anal.*, 11 (1977) 169.

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*Although the case $n = 1$ should be integrated in a different way, this case may be included in the following deduction; it is especially so when:

$$\lim_{n=1\pm\varepsilon\to 1} \sqrt[n-1]{\frac{1+(n-1)(1-\eta)}{n}} = e^{-1} \cdot (2 - \eta)$$