Journal of Thermal Analysis, Vol. 2 (1970) 459–460

Short communication

HYPERBOLIC TEMPERATURE VARIATION PROGRAM IN KINETIC INVESTIGATION

J. Zsakó

Faculty of Chemistry, Babeş-Bolyai University, Cluj, Rumania

(Received August 10, 1970)

A hyperbolic heating program enables us to integrate the general kinetic equation.

By following the kinetics of a simple homogeneous or heterogeneous reaction under non-isothermal conditions, it is possible to derive the activation energy E and the Arrhenius pre-exponential factor Z from a single kinetic curve. If at a given temperature the reaction rates of a homogeneous and of a heterogeneous reaction are

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = kf(c) \text{ and } \frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

(c stands for the concentration, α for the transformation degree of a reactant), and the rate constant k obeys the Arrhenius equation, the following differential equations are valid [1]:

$$-\frac{\mathrm{d}c}{f(c)} = Ze^{-E/RT}\psi'(T)\mathrm{d}T \text{ or } \frac{\mathrm{d}\alpha}{f(\alpha)} = Ze^{-E/RT}\psi'(T)\mathrm{d}T \qquad (2$$

In the case of a suitable temperature program the right hand side of Eq. (2) can be integrated. If the heating program performs a linear variation of $1/T$

$$1/T = a - qt \tag{3}$$

and we have

$$t = \psi(T) = \frac{1}{q}(a - 1/T) \quad \text{and} \quad \psi'(T)\mathrm{d}T = -\frac{1}{q}\mathrm{d}(1/T) \tag{4}$$

With this condition, Eq. (2) can be integrated as follows:

$$g(c) = -\int_{c_0}^{c} \frac{\mathrm{d}c}{f(c)} = -\frac{Z}{q}\int_{\infty}^{1/T} e^{-E/RT}\,\mathrm{d}(1/T) = \frac{ZR}{qE}\,e^{-E/RT}$$

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{ZR}{qE}\,e^{-E/RT} \tag{5}$$

By taking logarithms we obtain finally

$$\log g(c) = \log \frac{ZR}{qE} - \log \frac{E}{2.3R}\,\frac{1}{T}$$

$$\log g(\alpha) = \log \frac{ZR}{qE} - \log \frac{E}{2.3R}\,\frac{1}{T} \tag{6}$$

The graphical plot of log $g(c)$ or of log $g(\alpha)$ versus $1/T$ enables us to derive E and Z. If the reaction order is known, $g(c)$ or $g(\alpha)$ can easily be calculated from experimental data; if it is unknown, different reaction orders can be tried and the right one will ensure a good linearity according to Eq. (6).

The above procedure can be applied in both homogeneous systems (solutions) and heterogeneous ones (thermogravimetry).

*

The author thanks Mr. G. Niac for helpful discussions.

Reference

1. J. Zsakó, J. Thermal Anal., *2* (1970) 141.