Notes

ON THE DIFFERENCES BETWEEN LINEAR AND NON-LINEAR TEMPERATURE PROGRAMMES

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In a recent paper published in this Journal, special emphasis was given on the differences between non-isothermal kinetics with linear and non-linear programmes.

Supposing, as hypothesis [1], that:

$$\alpha = f(q, t), \quad \text{where} \quad q = \mathrm{d}T/\mathrm{d}t \tag{1}$$

it is obvious that the result of differentiation of Eq. (1) will also depend on q. Thus it is easy to admit that the form of the rate equation will depend on the form of the heating programme used, but this fact does not mean that the kinetics of the reaction itself will be different; that is no matter what the heating programme, one has to get the same values for A, E and n (if the model of the reaction order is accepted).

In fact, the time derivative of Eq (1) is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \left(\frac{\partial\alpha}{\partial q}\right)_t \cdot \frac{\mathrm{d}q}{\mathrm{d}t} \tag{2}$$

and, for the following forms of q, given by three different heating programmes:

– linear programme: $T = T_0 + at,\ q = a$ (3)

– exponential programme: $T = T_0 \exp bt,\ q = bT$ (4)

– hyperbolic programme:

$$\frac{1}{T} = \frac{1}{T_0} - ct, \quad q = cT^2 \tag{5}$$

Eq. (2) becomes:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_q \tag{2'a}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \left(\frac{\partial\alpha}{\partial q}\right)_t bq \tag{2'b}$$

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_q + \left(\frac{\partial \alpha}{\partial q}\right)_t 2cTq \tag{2'c}$$

However: 1. The exponential programme (4) can be rewritten as follows:

$$\ln \frac{T}{T_0} = \ln \left(1 + \frac{T - T_0}{T_0}\right) \simeq \frac{T - T_0}{T_0} = bt$$

which is a very good approximation for $\frac{T - T_0}{T_0} < 0.45$.

This approximation leads to:

$$T = T_0 + T_0 bt \tag{4'}$$

which is mathematically identical with Eq. (3).

2. Taking into account that $c \cong 10^{-4}$, the hyperbolic programme (5) can be rewritten in the form:

$$T = T_0 \frac{1}{1 - T_0 ct} \simeq T_0(1 + T_0 ct) \tag{5'}$$

which is also mathematically identical with Eq. (3).

In conclusion, both of the non-linear programmes can be reduced, as a first approximation, to a linear programme, and so one can account for the similitude of the experimental results for different heating programmes [2].

Hence, Eqs (2'a, b, c) express the same kinetics in different approximations.

References

1. V. M. Gorbachev, J. Thermal Anal., 20 (1981) 229.
2. H. Anderson, D. Haberland and E. Witte, J. Thermal Anal., 17 (1979) 409.