Note

A METHOD TO EVALUATE THE "REACTION ORDER" OF HETEROGENEOUS DECOMPOSITIONS UNDER NON-ISOTHERMAL CONDITIONS

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In the fundamental rate equation of non-isothermal kinetics [1,2]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} f(\alpha) \,\mathrm{e}^{-E/RT} \tag{1}$$

where all the notations have the known meanings, the "classical" conditions: A = ct; $E \doteq const.$; $f(\alpha) = (1 - \alpha)^n$, will be considered as fulfilled.

Let the value of the conversion degree at the temperature T_i , the sample being heated with the rate β_1 , be α_{1i} . The corresponding value of the conversion degree at T_i if the sample is heated with the rate β_2 will be denoted α_{2i} . The heating rates β_1 and β_2 will be chosen in such a way that $\beta_2 > \beta_1$.

Through variable separation and integration from eqn. (1) one obtains

$$\int_{\alpha_{1,i}}^{\alpha_{1,i}} \frac{\mathrm{d}\alpha}{\left(1-\alpha\right)^{n}} = \frac{A}{\beta_{1}} \int_{T_{i}}^{T_{i}} \mathrm{e}^{-E/RT} \mathrm{d}T$$
⁽²⁾

$$\int_{\alpha_{2_{\ell}}}^{\alpha_{2_{\ell}}} \frac{\mathrm{d}\alpha}{(1-\alpha)^{n}} = \frac{A}{\beta_{2}} \int_{T_{\ell}}^{T_{k}} \mathrm{e}^{-E/RT} \mathrm{d}T$$
(3)

By performing the integrations in the left-hand side of eqns. (2) and (3) and taking their ratio it turns out that

$$\frac{(1-\alpha_{2i})^{1-n}-(1-\alpha_{2k})^{1-n}}{(1-\alpha_{1i})^{1-n}-(1-\alpha_{1k})^{1-n}}=\frac{\beta_1}{\beta_2}$$
(4)

with

$$\beta_1 = \frac{T_k - T_i}{\Delta t_1} \tag{5}$$

and

$$\beta_2 = \frac{T_k - T_i}{\Delta t_2} \tag{6}$$

 Δt_1 and Δt_2 being the time intervals corresponding to the two heating rates. Relationships (4) is that searched for as it allows the "reaction order" to be evaluated.

The method was used for the dehydration of calcium oxalate monohydrate. The experimental data and the results were: $T_i = 433$ K, $T_k = 463$ K, $\beta_1 = 4.934$ K min⁻¹, $\beta_2 = 9.259$ K min⁻¹, $\alpha_{1i} = 0.1833$, $\alpha_{1k} = 0.8542$, $\alpha_{2i} = 0.1167$, $\alpha_{2k} = 0.6292$, n = 0.89. The value of n is in fairly good agreement with those given in the literature [3-5].

REFERENCES

- 1 E. Segal and D. Fătu, Introduction to Non-isothermal Kinetics, Publishing House of the Academy of the Socialist Republic of Romania, Bucharest, 1983, p. 76 (in Romanian).
- 2 J. Šesták, Thermophysical Properties of Solids, Academia, Prague, 1984, p. 218.
- 3 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
- 4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
- 5 E. Segal, Thermochim. Acta, 53 (1982) 365.