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Short Communications

ON SOME OBVIOUS CASES OF INCORRECT CHOICE OF THE RATE EQUATION FOR NON-ISOTHERMAL KINETICS

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In order to evaluate the non-isothermal kinetic parameters the following equation is used:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α stands for the degree of conversion, A – for the preexponential factor, E – for the activation energy, β – for the heating rate, T – for the temperature, R – for the universal gas constant, and $f(\alpha)$ – for the differential conversion function.

In order to find the form of the conversion function the following procedures have been suggested:

- The function $f(\alpha)$ is of the same analytical form as the corresponding function obtained from isothermal data [1–5].
- The optimal form of $f(\alpha)$ corresponds to the best linearization of the equation from which the activation parameters are obtained [6–8].
- The analytical form of $f(\alpha)$ is the one that leads to the same value of the preexponential factor for various linear heating rates [9].
- The correct analytical form of $f(\alpha)$ can be obtained from the DTG curve [10, 11].
- The correct analytical form of $f(\alpha)$ is that which leads to a value of the activation energy close to that obtained by means of an isoconversional method [12].

Recently [12], the extent of applicability of these procedures has been discussed.

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It has been shown [13–15] that for different kinetic models applied to the same non-isothermal thermoanalytical data, different values of the activation parameters have been obtained. These values proved to being correlated through the relationship:

$$\ln A = a + bE \tag{2}$$

where a and b are characteristic constants for the same kinetic data.
The validity of relationship (2) shows the existence of a compensation effect (*CE*) between the preexponential factor and the activation energy from the Arrhenius equation.

According to Criado and Gonzales [13], the method used for the evaluation of the kinetic parameters is a possible reason for the apparent compensation effect.

Nevertheless, as reported in references [13–15], for some analytical forms of $f(\alpha)$ applied to the same non-isothermal data, negative values of the activation energy are obtained. Among the examples we mention:

- for the decomposition of $PbCO_3$ and the model A_3, Criado and Gonzales [13] found E=–66.5 kJ mol^{-1}.
- for non-isothermal decomposition of $CaCO_3$ and:

$$f(\alpha) = (1-\alpha)^n\alpha^m[-\ln(1-\alpha)]^p \tag{3}$$

Adonyi and Kőrösi [14] using some sets of (n, m, p) obtained:

E_1= –10.16 kJ mol^{-1}; E_2=–102.92 kJ mol^{-1};
$E3$=–128.24 kJ mol^{-1}; E_4= –467.22 kJ mol^{-1}, etc.

- for the thermooxidative degradation of low density polyethylene, α values up to 0.74 and $f(\alpha)$ given by relationship (3), Vasile *et al.* [15] obtained for E values in the range –210 kJ mol^{-1}–180 kJ mol^{-1}.

All these values of the activation energy as well as the corresponding values of the preexponential factor are correlated through relationship (2), i.e. exhibit compensation effect. Nevertheless, negative values of the activation energy do not have any physical sense for the non-isothermal changes described by equation (1). Apparent negative values of the activation energy have been obtained for some gas phase reactions with preequilibrium like: $2NO+O_2 \rightarrow 2NO_2$ [16]. Coming back to the non-isothermal data it appears that negative values for the activation energy are due either to the wrong choice of $f(\alpha)$ or to a complex mechanism. Otherwise Vasile *et al.* [15] consider that the existence of such a compensation effect for the thermooxidation of low density polyethylene suggests a complex mechanism of mass loss.

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