Short Communication

FURTHER ASPECTS OF THE KINETIC COMPENSATION EFFECT

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Mathematical considerations are used to show that the existence of an isokinetic point does not always indicate the kinetic compensation effect as a result of physicochemical reasons. The correlation of the Arrhenius parameters is given for both the inappropriate kinetic model function and the working temperature interval.

The kinetic compensation effect (KCE) for solid-state reactions has been discussed as a linear interdependence between the apparent activation energy, $E$, and the logarithm of the pre-exponential factor, $A$, and is expressed by the following equation [1-3]:

$$\ln A = \frac{E}{RT_{iso}} + \ln k (T_{iso})$$  \hspace{1cm} (1)

where $R$ is the gas constant, $T_{iso}$ is the isokinetic temperature and $k$ is the rate constant. The simple relationship of Eq. (1) can be understood as a

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The mathematical consequence of the exponential form of the rate constant in the Arrhenius equation [1, 4, 5] and seems to arise from a projection of the interrelationship between lnA, E and temperature, T, terms to the lnA vs. E coordinate [6], although the physical meaning of $T_{iso}$ has not fully been solved as yet. It is interesting to shed light mathematically on the relationship between the KCE and the T terms. From this point of view, the KCE can be divided into two categories according to whether the KCE is accompanied by changes in the T terms or not [7].

The KCE arising from a single nonisothermal thermoanalytical (TA) curve by the use of various inappropriate kinetic model functions is one of the examples where the T terms remain constant. This KCE has been discussed from empirical [8–11] and mathematical [6, 12] aspects. Somasekharan and Kalpagam reported [13] that in this type of KCE the $T_{iso}$ closely corresponds to the peak temperature, $T_p$, of the TA curve.

For a single TA curve at a given heating rate, $\Phi$, the mathematical condition for the peak can be written as [14]

$$\frac{\Phi E}{RT_p^2} - F(\alpha_p) \cdot A \exp \left( - \frac{E}{RT_p} \right) = 0 \tag{2}$$

with

$$F(\alpha_p) = - \left[ \frac{df(\alpha)}{d\alpha} \right] \alpha = \alpha_p \tag{3}$$

where $f(\alpha)$ is the kinetic model function and $\alpha_p$ is the fractional conversion at $T_p$. Rearrangement of Eq. (2) gives [6]

$$\ln A = \frac{E}{RT_p} + \ln \left[ \frac{\Phi}{R} \cdot \frac{1}{T_p^2} \cdot F(\alpha_p) \right] \tag{4}$$

If a false kinetic model function, $h(\alpha)$, was used instead of the appropriate one, $f(\alpha)$, Eq. (4) can be rewritten as

$$\ln A_{app} = \frac{E_{app}}{RT_p} + \ln \left[ \frac{E_{app}}{R} \cdot \frac{\Phi}{T_p^2} \cdot H(\alpha_p) \right] \tag{5}$$

with