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]:

$$\ln A = \frac{E}{RT_{\text{iso}}} + \ln k \, (T_{\text{iso}}) \tag{1}$$

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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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 $\ln A$, E and temperature, T, terms to the $\ln A$ 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, Φ, 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 α_p is the fractional conversion at T_p. Rearrangement of Eq. (2) gives [6]

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

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

$$\ln A_{app} = \frac{E_{app}}{RT_p} + \ln\left[\frac{E_{app}}{R} \cdot \frac{\Phi}{T_p^2} \cdot \frac{1}{H(\alpha_p)}\right] \tag{5}$$

with

$$H(\alpha_p) = - \left[\frac{dh(\alpha)}{d\alpha}\right]\alpha = \alpha_p \tag{6}$$

where A_{app} and E_{app} are the apparent pre-exponential factor and activation energy distorted by the use of $H(\alpha_p)$. From a combination of Eq. (4) with Eq. (5):

$$\Delta \ln A = \frac{\Delta E}{RT_p} + \ln \left[\frac{F(\alpha_p)}{H(\alpha_p)} \cdot \frac{E_{app}}{E}\right] \tag{7}$$

where $\Delta \ln A = \ln A_{app} - \ln A$ and $\Delta E = E_{app} - E$. According to the previous study [15], the distortion of the E value, E_{app}/E, can be expressed by

$$\frac{E_{app}}{E} = \frac{f(\alpha_p)}{h(\alpha_p)} \cdot \frac{H(\alpha_p)}{F(\alpha_p)} \tag{8}$$

Replacing the term E_{app}/E in Eq. (7) by Eq. (8), we get [6]

$$\Delta \ln A = \frac{\Delta E}{RT_p} + \ln \frac{f(\alpha_p)}{h(\alpha_p)} \tag{9}$$

When the logarithmic terms in Eqs (7) and (9) are close to zero, the plot of $\ln A$ vs. E has a slope of $1/RT_p$. Since the values of the logarithmic terms change with $h(\alpha_p)$, the slope differs from $1/RT_p$, depending on the $h(\alpha_p)$ used. In the case of establishing the KCE with the use of various $h(\alpha_p)$, the slope of the plot of KCE is a certain mean value determined from the relationship between the $f(\alpha_p)$ and $h(\alpha_p)$ examined. This explains the empirical fact that the KCE of this type does not indicate a single intersecting point on the Arrhenius coordinate, i.e. an isokinetic point [16]. Accordingly, it is sometimes called a 'false' and/or 'superficial' KCE.

On the other hand, in the case of a KCE established between the Arrhenius parameters obtained from more than one TA curve under various sample and measuring conditions, the changes in the values of E and $\ln A$ are always accompanied by a change in the reaction temperature region. This also holds for isothermal analysis, because the working temperature interval is sometimes restricted by the practical requirements relating to the sample and measuring conditions. A fundamental analysis of the angle θ on the Arrhenius coordinate, i.e. E/R, clearly suggests that the value of E depends not only on the reaction temperature, but also on the working

temperature interval, ΔT [1, 4, 5]. In addition, the linear interdependence of E and/or $\ln A$ and $1/\Delta T$ is suggested from an empirical point of view [7, 17].

For the values of E and A obtained from the respective methods of kinetic analysis, the following relationships can be derived by using the lowest temperature, T_L, the highest temperature, T_H, and $\Delta T = T_H - T_L$.

(i) Isothermal methods:

$$E = \frac{RT_HT_L}{\Delta T} \cdot \ln \frac{\dot{\alpha}_H}{\dot{\alpha}_L} \tag{10}$$

$$\ln A = \frac{1}{T_{iso}} \cdot \frac{T_HT_L}{\Delta T} \cdot \ln \frac{\dot{\alpha}_H}{\dot{\alpha}_L} + \ln k(T_{iso}) \tag{11}$$

where $\dot{\alpha}$ is $d\alpha/dt$ and the subscripts H and L denote the values at T_H and T_L, respectively.

(ii) Non-isothermal single run methods [18]:

$$E = \frac{RT_HT_L}{\Delta T} \cdot \ln \left[\frac{(d\alpha/dT)_H}{(d\alpha/dT)_L} \cdot \frac{f(\alpha_L)}{f(\alpha_H)} \right] \tag{12}$$

$$\ln A = \frac{1}{T_{iso}} \cdot \frac{T_HT_L}{\Delta T} \cdot \ln \left[\frac{(d\alpha/dT)_H}{(d\alpha/dT)_L} \cdot \frac{f(\alpha_L)}{f(\alpha_H)} \right] + \ln k(T_{iso}) \tag{13}$$

(iii) Non-isothermal multi-heating rate methods [19, 20]:

a) Isoconversion methods [19, 20]

$$E = \frac{RT_HT_L}{\Delta T} \cdot \ln \left[\frac{(d\alpha/dT)_H}{(d\alpha/dT)_L} \cdot \frac{\Phi_H}{\Phi_L} \right] \tag{14}$$

$$\ln A = \frac{1}{T_{iso}} \cdot \frac{T_HT_L}{\Delta T} \cdot \ln \left[\frac{(d\alpha/dT)_H}{(d\alpha/dT)_L} \cdot \frac{\Phi_H)}{\Phi_L)} \right] + \ln k(T_{iso}) \tag{15}$$

b) Peak methods [21]:

$$E = \frac{RT_HT_L}{\Delta T} \cdot \ln \left[\frac{F(\alpha_L)}{F(\alpha_H)} \cdot \frac{T_L^2}{T_H^2} \cdot \frac{\Phi_H}{\Phi_L} \right] \tag{16}$$

$$\ln A = \frac{1}{T_{\text{iso}}} \cdot \frac{T_H T_L}{\Delta T} \cdot \ln\left[\frac{F(\alpha_L)}{F(\alpha_H)} \cdot \frac{T_L^2}{T_H^2} \cdot \frac{\Phi_H)}{\Phi_L)}\right] + \ln k\,(T_{\text{iso}}) \qquad (17)$$

Since the changes in the logarithmic terms in Eqs (10), (12), (14) and (16) accompanying the change in reaction temperature region are small compared with the change in the value of $T_H T_L/\Delta T$, the values of E and $\ln A$ must be functions of $T_H T_L/\Delta T$. This implies that a constant value of $T_H T_L/\Delta T$ is a necessary condition for a constant E value [22]. In this case, however, a constant value of $\ln A$ is not necessarily obtained. From this empirical fact [7], constant Arrhenius parameters are obtained for a constant value of ΔT. This is explained by the present mathematical consequence that, for a smaller ΔT, even the change in $T_H T_L$ can be ignored in comparison with the change in $1/\Delta T$. For the same reason, the values of E and $\ln A$ must be functions of $1/\Delta T$, when the KCE is established between these Arrhenius parameters. If the change in $1/\Delta T$ were systematic, the existence of the isokinetic point would be observed, provided the kinetic model function remains unchanged [23–25]. In this respect, the existence of the isokinetic point does not always indicate the KCE that arises for some physicochemical reason, because the experimental error in thermoanalytical measurements is sometimes systematic [26].

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