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Note

SHORT COMMENTS ON KINETIC MODELS INVOLVING CHANGES IN ACTIVATION ENERGY

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In a paper which earlier appeared in this journal [1], Malecki and co-workers applied a kinetic model based on the assumption that the activation energy changes as a function of temperature T and a degree of conversion α. The non-constant activation energy E_t was calculated via the following equation (see formulae (16) and (17) in Ref. [1]):

$$E_t = E_0 + Tf_0(\alpha) \tag{1}$$

where E_0 is a positive constant, and $f_0(\alpha)$ is an appropriately selected real function. It is worthwhile to note that the same equation was used in a much earlier paper [2].

In this short communication, we present a critical analysis of the mathematical treatment of Eq. (1), and show that the hypothesis involved in Eq. (1) leads to a false and quite complicated interpretation of the kinetics of the reaction investigated.

Our concept and arguments are based on the following considerations: As a first step, let us re-write Eq. (1) in an equivalent form:

$$E_t = E_0 + RTf_1(\alpha) \tag{2}$$

where R is the universal gas constant, and function $f_1(\alpha)$ is defined as $f_1(\alpha)=f_0(\alpha)/R$. As a second step, let us consider the non-isothermal kinetic differential equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_0 \exp\left(-\frac{E_t}{RT}\right) g_1(\alpha) = k_0 \exp\left[-\frac{E_0 + RTf_1(\alpha)}{RT}\right] g_1(\alpha) \tag{3}$$

In Eq. (3), t is the time, the term E_t is defined by Eq. (2), k_0 is the pre-exponential coefficient, and $g_1(\alpha)$ is an arbitrarily selected conversion function.

Next, let us define a new conversion function:

$$g_2(\alpha) = g_1(\alpha)\exp[-f_1(\alpha)] \tag{4}$$

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After the insertion of formula (4) into Eq. (3), the transformation rate Eq. (3) can be described in the following modified form:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=K(T)g_2(\alpha) \tag{5}$$

where $K(T)$ is the Arrhenius formula given as

$$K(T)=k_0\exp\left(-\frac{E_0}{RT}\right) \tag{6}$$

and E_0 is the constant activation energy of the reaction. Integration of the differential Eq. (5) leads to the following solution:

$$\alpha(t)=G^{-1}\left[\int_0^t k_0\exp\left(-\frac{E_0}{RT}\right)\mathrm{d}t\right] \tag{7}$$

where G^{-1} is the inverse of function $G=G(\alpha)$, defined as

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{g_2(\alpha)} \tag{8}$$

From Eqs (2)–(8), the following conclusions can be drawn:

i. It follows from Eq. (4) that functions $g_1(\alpha)$ and $g_2(\alpha)$ are not independent. Consequently, the conversion equation $g_2(\alpha)$ can be directly calculated as a function of $g_1(\alpha)$. Due to this fact, although kinetic Eqs (3) and (5) are apparently of a different type, they are considered to be equivalent.

ii. Transformation processes described by kinetic Eqs (3) and (5) possess the same constant activation energy E_0. In other words, activation energy E_0 characterizing both reactions is independent of the particular choice of functions $g_1(\alpha)$ or $g_2(\alpha)$. This implies that, instead of the correct and simple Eq. (5), it is superfluous and not advisable to use the more complicated kinetic model represented by Eqs (2) and (3).

In order to illustrate the practical application of the mathematical transformation formulated by Eq. (4), let us consider the following example.

Let us define functions $g_1(\alpha)$ and $f_1(\alpha)$:

$$g_1(\alpha)=(1-\alpha)^{\mathrm{n}} \tag{9}$$

$$f_1(\alpha)=p\ln\frac{1}{1-\alpha}=-p\ln(1-\alpha) \tag{10}$$

In Eqs (9) and (10), parameters n and p are constant and the inequalities $n\geq1$ and $p\geq0$ hold. In this case, Eq. (2) can be reduced to the form $E_t=E_0-pT\ln(1-\alpha)$.

From Eqs (4), (8), (9) and (10), we have

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{g_2(\alpha)}=\int_0^\alpha\frac{\mathrm{d}\alpha}{(1-\alpha)^{\mathrm{n+p}}} \tag{11}$$

where $n+p\geq 1$ is valid.

After integration, we obtain

$$G(\alpha)=\begin{cases}-\ln(1-\alpha) & \text{for } n=1 \text{ and } p=0\\ \dfrac{1}{1-n-p}[1-(1-\alpha)^{1-n-p}] & \text{for } n+p>1\end{cases} \tag{12}$$

Starting with Eqs (9)–(12), we obtain the solution of the differential Eq. (5) in the following final form:

$$\alpha(t)=\begin{cases}1-\exp\left[-\int\limits_0^t K(T)\mathrm{d}t\right] & \text{for } n=1 \text{ and } p=0\\ 1-[1-(1-n-p)\int\limits_0^t K(T)\mathrm{d}t]^{\frac{1}{1-n-p}} & \text{for } n+p>1\end{cases} \tag{13}$$

where $K(T)$ is defined by Eq. (6).

It can be concluded that theoretically it is possible to imagine a completely new and physically well-founded kinetic model based on the assumption of a non-constant activation energy, but the use of Eq. (1) does not lead closer to a solution to this problem.

References

1 A. Małecki, B. Prochowska-Klisch and R. Gajerski, J. Therm. Anal. Cal., 54 (1998) 25.
2 A. Małecki and J. P. Doumerc, J. Thermal Anal., 31 (1986) 567.