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LINEAR AND HYPERBOLIC TEMPERATURE PROGRAMMING IN NON-ISOTHERMAL KINETICS

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The method suggested by several authors for determining the mechanism of solid-phase transformations by linearizing the function $\ln g(\alpha)$ *vs.* $\frac{1}{T}$ is more correct for a hyperbolic temperature change than for a linear temperature change. In the latter case, the method yields reliable results only under the condition that the relationship $\ln \frac{g(\alpha)}{T^2}$ *vs.* $\frac{1}{T}$ is linear. The well-known Horowitz–Metzger method is essentially suited for processing thermokinetic curves obtained under hyperbolic heating or cooling.

In the practice of thermal analysis, linear temperature programming $T = T_0 + at$ is usually applied. A hyperbolic temperature change [1, 2] $1/T = 1/T_0 - bt$ is much less frequent. However, in some cases of thermokinetic analysis it is desirable, for in the case of a hyperbolic temperature change the integration of the differential equations in non-isothermal kinetics is much simpler [1, 3].

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

$$\int\limits_{T_0}^{T} \frac{d\alpha}{f(\alpha)} = g_b(\alpha) = \frac{AR}{bE_b}\left\{\exp\left(-\frac{E_b}{RT}\right) - \exp\left(-\frac{E_b}{RT_0}\right)\right\} \tag{2}$$

For the case of linear heating $T = T_0 + at$, integration of Eq. (1) using the solution of the temperature integral proposed by us [4] yields

$$g_a(\alpha) = \frac{AR}{a}\left\{\frac{T^2}{E_a + RT}\exp\left(-\frac{E_a}{RT}\right) - \frac{T_0^2}{E_a + RT_0}\exp\left(-\frac{E_a}{RT_0}\right)\right\} \tag{3}$$

For convenience in the subsequent mathematical considerations, let us assume that $T \gg T_0$. Then

$$g_b(\alpha) = \frac{AR}{bE_b}\exp\left(-\frac{E_b}{RT}\right) \tag{4}$$

$$g_a(\alpha) = \frac{ART^2}{a(E_a + 2RT)}\exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

Let us write Eq. (5) for linear heating in the form proposed by Satava [5] and Satava and Skvara [6]:

$$g_a(\alpha) = \frac{AE_a}{aR}\left\{\frac{R^2T^2}{E_a(E_a + 2RT)}\exp\left(-\frac{E_a}{RT}\right)\right\} = \frac{AE_a}{aR}p(x) \tag{6}$$

$$\ln g_a(\alpha) - \ln p(x) = \ln\frac{AE_a}{aR} \tag{7}$$

Obviously, the function $\ln p(x)$ in Eq. (7) is not linearly related to reciproca temperature. Therefore, the assumption that the function $\ln g_a(\alpha)$ is in a linear relationship to reciprocal temperature is not true, and hence the method proposed by a number of authors [5, 6 and others] for finding the initial function $f(\alpha)$ by linearizing the set of functions $\ln g_a(\alpha)$ against reciprocal temperature is not quite accurate. It appears that this method for processing kinetic information obtained by linear heating will yield reliable results under the condition that $\ln\frac{g_a(\alpha)}{T^2}$ *vs.* $\frac{1}{T}$ is linear. A hyperbolic temperature change, on the other hand, corresponds ideally to this method to find the initial function $f(\alpha)$ and $g(\alpha)$. In this case,

$$\ln g_b(\alpha) + \frac{E_b}{RT} = \ln\frac{AR}{bE_b} \tag{8}$$

However, in all cases it must be considered that the widely used Arrhenius model $K = A\exp\left(-\frac{E}{RT}\right)$ is only an approach [7, 8], and a particular case of the more general kinetic law $K = AT^B\exp\left(-\frac{E_0}{RT}\right)$, and this must necessarily be reflected in the form of the wanted function $f(\alpha)$ or $g(\alpha)$.

Let us analyze Eqs (4) and (5) using the functions $f(\alpha) = (1 - \alpha^\eta)$ or $(1 - \alpha)^n$. Here η is the order of the reaction on hyperbolic heating, and n the order of the reaction on linear heating. Utilizing Eq. (4), we can write

$$\frac{1-(1-\alpha)^{1-\eta}}{1-\eta} = \frac{AR}{bE_b}\exp\left(-\frac{E_b}{RT}\right) \tag{9}$$

The factor A can be found by using the method proposed earlier by us [9]. This finally yields

$$A = \frac{E_b b}{R}\,\frac{(1-\alpha_s)^{1-\eta}}{\eta}\exp\left(\frac{E_b}{RT_s}\right) \tag{10}$$

where the subscript s refers to the point where the rate of the non-isothermal transformation is maximum. Let us now write Eq. (9) in its full form:

$$\frac{1-(1-\alpha)^{1-\eta}}{1-\eta} = \frac{(1-\alpha_s)^{1-\eta}}{\eta}\exp\left(\frac{E_b}{RT_s}\right)\exp\left(-\frac{E_b}{RT}\right) \tag{11}$$

At the point (α_s, T_s)

$$\frac{1-(1-\alpha_s)^{1-\eta}}{1-\eta} = \frac{(1-\alpha_s)^{1-\eta}}{\eta} \quad \text{or} \quad (1-\alpha_s)^{1-\eta} = \eta \tag{12}$$

Hence Eq. (11) assumes the form

$$\frac{1-(1-\alpha)^{1-\eta}}{1-\eta} = \exp\left(\frac{E_b}{RT_s}\right)\exp\left(-\frac{E_b}{RT}\right) \tag{13}$$

Equations (12) and (13) essentially agree with the expressions of Horowitz and Metzger [10] proposed for processing thermokinetic curves involving linear heating, assuming that $T_sT \approx T_s^2$.

Let us now carry out similar mathematical transformations with Eq. (5) for linear heating, again assuming that $T \gg T_0$. The final result is

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{(1-\alpha_s)^{1-n}}{n}\left(\frac{T}{T_s}\right)^2\left(\frac{E_a}{E_a+2RT}\right)\exp\left(\frac{E_a}{RT_o}\right)\exp\left(-\frac{E_a}{RT}\right) \tag{14}$$

At the same extreme point (α_s, T_s) we obtain

$$\frac{1-(1-\alpha_s)^{1-n}}{1-n} = \frac{(1-\alpha_s)^{1-n}}{n}\left(\frac{E_a}{E_a+2RT_s}\right)$$

or

$$(1-\alpha_s)^{1-n} = 1 + \frac{1-n}{n}\left(\frac{E_a}{E_a+2RT_s}\right) \tag{15}$$

Equation (15) will approach the known relationship $(1-\alpha_s)^{1-n} = n$ only at very large values of E_a. This equation shows that in the general case the effective order of reaction n for linear heating is modified by the values E_a and T_s. In [11] an empirical formula accounting for this modification is given:

$$1-\alpha_s = 1.062\, n^{\frac{1}{1-n}} \tag{16}$$

This relationship is illustrated in Fig. 1 of the cited paper [11] where, at $1-\alpha_s = 0.5$, the value of η is 2, while that of n is 1.70. This condition may lead to substantial differences between E_a and E_b under otherwise equal conditions.

Finally, it should be pointed out that the described procedure for finding the order of reaction η or n from the thermokinetic curves is correct under the condition that $T_s \gg T_0$. This can be shown by the example of a transformation under hyperbolic heating:

$$\frac{1-(1-\alpha_s)^{1-\eta}}{1-\eta} = \frac{(1-\alpha_s)^{1-\eta}}{\eta}\left\{1-\exp\left(\frac{E_b}{RT_s}\right)\exp\left(-\frac{E_b}{RT_0}\right)\right\}$$

It is obvious that the absolute value of the multiplication factor between the figure brackets depends on the starting temperature T_0, so that a change in this value will be reflected in η at $E_b = \text{const}$.

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Résumé — La méthode proposée par plusieurs auteurs pour déterminer le mécanisme des transformations en phase solide en linéarisant la fonction reliant $\ln g(\alpha)$ et $1/T$ est plus correcte lorsque les variations de température suivent un régime hyperbolique qu'elle ne l'est pour les régimes linéaires. Dans ce dernier cas, la méthode ne fournit des résultats fiables qu'à la condition que la relation entre $\ln g(\alpha)/T^2$ et $1/T$ soit linéaire. La méthode bien connue d'Horowitz–Metzger s'applique essentiellement au traitement des courbes obtenues avec des lois d'échauffement ou de refroidissement hyperboliques.

Zusammenfassung — Die von mehreren Autoren vorgeschlagene Methode den Mechanismus von Umwandlungen in der Festphase durch Linearisierung der Funktion zwischen $\ln g(\alpha)$ und $1/T$ zu bestimmen ist für hyperbolische Temperaturänderungen korrekter als für die lineare Temperaturänderung. In letzterem Falle ergibt die Methode nur unter der Bedingung zuverlässige Ergebnisse, daß der Zusammenhang zwischen $\ln g(\alpha)/T^2$ und $1/T$ linear ist. Die bekannte Methode nach Horowitz—Metzger eignet sich im Wesentlichen zur Bearbeitung thermokinetischer Kurven bei hyperbolischem Aufheizen oder Kühlen.

Резюме — Предложенный рядом авторов метод установления механизма твердофазного превращения путем линеаризации функции $\ln g(\alpha)$ vs $1/T$ более корректен для гиперболического закона изменения температуры, для линейного закона этот метод может давать надежные результеты только при условии линейности $\ln g(\alpha)/T^2$ vs $1/T$. Широко известный метод Горовитца — Метцгера по существу предназначен для обработки термокинетических кривых при гиперболическом законе нагревания или охлаждения.