LINEAR AND HYPERBOLIC TEMPERATURE PROGRAMMING IN NON-ISOTHERMAL KINETICS

V. M. GORBACHEV

Institute of Inorganic Chemistry, Siberian Department of the Academy of Sciences of the U.S.S.R., Novosibirsk 630090

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The method suggested by several authors for determining the mechanism of solid-phase transformations by linearizing the function \( \ln g(x) \) 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 \( \frac{g(x)}{T^2} \) 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 \( \frac{1}{T} = \frac{1}{T_0} - bt \) 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].

\[
\frac{dx}{dt} = A e^{-E/RT} f(x) 
\]

\[
\int_{T_0}^{T} \frac{dx}{f(x)} = g_b(x) = \frac{AR}{bE_b} \left\{ \exp \left( - \frac{E_b}{RT} \right) - \exp \left( - \frac{E_b}{RT_0} \right) \right\} 
\]

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

\[
g_d(x) = \frac{AR}{a} \left\{ \frac{T^2}{E_a + RT} \exp \left( - \frac{E_a}{RT} \right) - \frac{T_0^2}{E_a + RT_0} \exp \left( - \frac{E_a}{RT_0} \right) \right\} 
\]

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

\[
g_b(x) = \frac{AR}{bE_b} \exp \left( - \frac{E_b}{RT} \right) 
\]

\[
g_d(x) = \frac{ART^2}{a(E_a + 2RT)} \exp \left( - \frac{E_a}{RT} \right) 
\]
Let us write Eq. (5) for linear heating in the form proposed by Satava [5] and Satava and Skvara [6]:

\[ g_a(x) = \frac{A E_a}{a R} \left( \frac{R^2 T^2}{E_a(E_a + 2RT)} \right) \exp \left( -\frac{E_a}{RT} \right) = \frac{A E_a}{a R} p(x) \]  

(6)

\[ \ln g_a(x) - \ln p(x) = \ln \frac{A E_a}{a R} \]  

(7)

Obviously, the function \( \ln p(x) \) in Eq. (7) is not linearly related to reciprocal temperature. Therefore, the assumption that the function \( \ln g_a(x) \) 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 \( f(x) \) by linearizing the set of functions \( \ln g_a(x) \) 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 \( \ln \frac{g_a(x)}{T^2} \) vs. \( \frac{1}{T} \) is linear. A hyperbolic temperature change, on the other hand, corresponds ideally to this method to find the initial function \( f(x) \) and \( g(x) \). In this case,

\[ \ln g_b(x) + \frac{E_b}{RT} = \ln \frac{AR}{bE_b} \]  

(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 \( K = AT^\eta \exp \left( -\frac{E_0}{RT} \right) \), and this must necessarily be reflected in the form of the wanted function \( f(x) \) or \( g(x) \).

Let us analyze Eqs (4) and (5) using the functions \( f(x) = (1 - x^n) \) or \( (1 - x)^n \). Here \( \eta \) 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

\[ \frac{1 - (1 - x)^{1 - \eta}}{1 - \eta} = \frac{AR}{bE_b} \exp \left( -\frac{E_b}{RT} \right) \]  

(9)

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

\[ A = \frac{E_b b}{R} \frac{(1 - x_s)^{1 - \eta}}{\eta} \exp \left( \frac{E_b}{RT_s} \right) \]  

(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:

\[ \frac{1 - (1 - x)^{1 - \eta}}{1 - \eta} = \frac{(1 - x_s)^{1 - \eta}}{\eta} \exp \left( \frac{E_b}{RT_s} \right) \exp \left( -\frac{E_b}{RT} \right) \]  

(11)