

ON CORRECTNESS OF THE DERIVATOGRAPHIC EXPERIMENT

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ALSTRACT

The influence of experimental conditions on the kinetic parameters of chemical transformation has been analysed with regard to the phenomenon of heat transfer. A more rigorous approach to the derivatographic experiment with a corresponding selection of experimental conditions has been shown.

INTRODUCTION

Thermogravimeters of different types are now widely used to study the kinetics of chemical transformation. The curves obtained experimentally by the differential thermal analysis (DTA) contain a series of values of time dependences from which it is possible to obtain kinetic parameters of the transformation; the activation energy E and the jump of enthalpy ΔH are the most important. It is quite natural to consider that these parameters are typical for a definite chemical transformation though when comparing the references it does not seem so. As for example, experimentally obtained magnitudes of activation energy for the decomposition of calcium carbonate vary from 19 to 96 kcal/mol [1-8]. Such varieties, observed for most of chemical transformations give the idea that it is impossible to determine values of the activation energy experimentally [9].

It can be concluded from our experiments of the decomposition of carbonates and experiments described by other authors [2,6,10-13] that the process of chemical transformation is strongly affected by experimental conditions, i.e. the rate of linear heating, weight, the size of grains of the substance under investigation and even by the form and size of the crucible. Consequently, in case of mathematical processing of DTA curves the experimental conditions must be not overlooked. This is the problem the present paper deals with.

RESULTS AND DISCUSSION

During the experiment the substance under investigation occupies a part of the crucible, though the temperature is taken at one point only (in most cases the thermocouple is connected with the crucible thus fixing the temperature of the crucible). Obviously it is wrong to ascribe this temperature to the whole substance. In different microareas of the substance its temperature depends on the distance from the heat source and the heat transfer factor. In the most ordinary case, i.e. if in the substance under investigation there are no local heat sources or heat absorbers, and the heat transfer coefficient, the specific heat and the density of the substance do not depend on the temperature, then the heat transfer can be described by the equation of heat transfer

$$\frac{\partial T}{\partial t} = a^2 \Delta T, \quad (1)$$

where a^2 - ratio of the heat transfer coefficient to the specific heat and density. The initial conditions must be added to the equation (1)

$$T|_{t=0} = T_H, \quad (2)$$

where T_H is the temperature at the beginning of the experiment and the boundary requirements

$$T|_S = T_H + \dot{\gamma} t, \quad (3)$$

where $\dot{\gamma}$ - the rate of linear heating.

The surface S of the volume of substance under investigation is determined by the form and size of the crucible and by the degree the crucible is filled up with the substance. There is no problem in solving the equations (1-3) [14] and we can show that for any form and size of the volume of substance under investigation the solution is

$$T = T_H + \dot{\gamma} t - \dot{\gamma} \frac{G(P, t)}{a^2}, \quad (4)$$

where $G(P, t)$ is a function which depends on the coordinate P characterizing the lay-out of the grains and the microareas of the substance and time. The analytical display of the function depends on the form of the volume to be investigated.

To explain the time dependence of the temperature fixed during the experiment and the temperature in the point with the coordinates P we must look at the first approximation of the function $G(P, t)$

$$G(P, t) \approx G_0(P) \left(1 - e^{-\frac{\pi^2 a^2 t}{l^2}} \right); \quad (5)$$

where l is the linear size of the volume. It is obvious that on the condition $t \gg l^2 / (\pi^2 a^2)$ the exponential part in the equation (5) is practically equal to zero and $G(P, t) = G_0(P)$; then the equation (4) looks like

$$T = T_H + \gamma t - \gamma \frac{G_0(P)}{a^2}. \quad (6)$$

For most substances in the solid state the factor a^2 is with magnitude about $10^{-3} \text{ cm}^2/\text{s}$; however, for unpressed powders of the same materials a^2 reaches about $10^{-4} + 10^{-5} \text{ cm}^2/\text{s}$.

A question arises how the temperature gradient influences the kinetic parameters of chemical transformation of the volume of substance under investigation. For example, let us analyse the dependence of the degree of transformation on the temperature from which it is possible to determine the activation energy. As the experimentally fixed temperature T_g changes lineary, then the temperature of any particle or microarea of the substance will be described by the equation

$$T = T_g - \gamma \frac{G(P, t)}{a^2} \quad (7)$$

and if the degree of transformation everywhere in the volume under investigation is determined by the same rule $\alpha = \alpha(T)$, then the degree of transformation for the whole volume will be

$$\alpha(T_g) = \frac{1}{V_0} \iiint_V V(P) \alpha \left(T_g - \gamma \frac{G(P, t)}{a^2} \right) dP, \quad (8)$$

where V_0 - volume of the whole substance, $V(P)$ - volume of the particle or microarea with the coordinates P . As the activation energy is obtained from the experimentally determined dependence $\alpha = \alpha(T_g)$; then in accordance with the equation (8) the activation energy depends on the rate of linear heating and coefficient a^2 , which in its turn depends on the coefficient of heat transfer, the specific heat and the density of the substance and on the function $G(P, t)$ depending on the form and size of the crucible and weight.

CONCLUSIONS

It has been shown that even the most ordinary account of the heat transfer allows us to interpret the influence of experimental conditions on the value of kinetic parameters of chemical transformation. However, at the same time the methodology of determination of kinetic parameters in accordance with the equation (8) becomes really complicated and it is impossible to do without a computer.

Another way how to lessen the effect of experimental conditions is to select them more carefully. Practically it means to realize the equation

$$t \gg \frac{G(P,t)}{a^2} . \quad (9)$$

Therefore it is necessary to know the specific heat, the coefficient of the heat transfer and the density of substance, and to state the function $G(P,t)$ characterizing the form of the crucible and the volume occupied by the substance in the crucible.

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