INVESTIGATIONS UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS BY MEANS OF THE DERIVATOGRAPH

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It is proved that under the conditions of dynamic thermoanalytical examinations the course of a decomposition reaction is determined primarily by the gas- and heat-transfer partial processes, i.e. indirectly by the experimental conditions. This raises the question of whether it is justified to make kinetic calculations based on the shapes of similar curves. A new measuring technique is reported which uses a slightly modified Derivatograph. With this new method decomposition reactions can be examined under "quasi-isothermal" and "quasi-isobaric" conditions. The pernicious effects of the gas- and heat-transfer processes are thus eliminated, and the shapes of the curves obtained provide the possibility of studying the decomposition reactions in a new and more thorough way.

It seems evident that the results of thermoanalytical examinations can be used to draw conclusions on the kinetics and possibly the mechanism of reactions leading to equilibrium. Accordingly, many approximate calculation methods have been elaborated for the determination of reaction order and activation energy. Despite the perfect logic upon which these calculations were generally based, they did not always fulfill expectations. This is due in part to the fact that the thermal curves used for the calculations very often gave a distorted picture of the transformation processes.

Thermal decomposition reactions leading to equilibrium consist of a number of chemical and physical partial processes. These partial processes are usually interdependent on each other in a complex way. Table 1 gives a schematic picture of the correlations. The course of the reaction is determined by the rate of the slowest partial process. If this is commensurable with the heating rate applied, then the transformation with increasing temperature will take place with delay over a more or less broad temperature interval.

Of the many partial processes, only two may be regarded as really chemical. One takes place at the interface as demonstrated in Fig. 1. This process is the release of gas molecules from the lattice and their rebuilding into it. The other is the chemisorption and desorption of gas molecules at the interface. Since both of these processes leading to equilibrium take place extremely rapidly, they do not usually influence the course of the transformation.

Nucleus formation and nucleus growth may be regarded as a transition between chemical and physical processes. Simultaneously with the departure of the gas
Table 1
Partial processes in thermal decomposition reactions leading to equilibrium

- Evolution of gaseous products
  - release \( \rightleftharpoons \) return of gas molecules from or to the lattice, respectively
  - chemisorption \( \rightleftharpoons \) desorption of the gas molecules at the interface

- Departure of gaseous products by diffusion
  - through the capillaries of the grain, between interface \( \rightleftharpoons \) grain boundary
  - through the space unfilled with grain, between grain boundary \( \rightleftharpoons \) sample surface
  - in the sample holder between sample surface \( \rightleftharpoons \) surroundings

- Formation of new solid phase
  - Nucleus formation
  - Growth of nucleus
  - Recrystallization

- Heat transfer
  - between surface \( \rightleftharpoons \) centre of a single grain
  - between surface \( \rightleftharpoons \) centre of the sample
  - between furnace \( \rightleftharpoons \) sample surface

Relation between the rate of the partial process and the heating program applied
- quicker, therefore not rate-determining
- comparable, therefore may be rate-determining
- slower, therefore in most cases rate-determining