Journal of Thermal Analysis, Vol. 33 (1988) 1267—1268

THERMAL ANALYSIS AND KINETIC CONCEPTS OF SOLID-STATE REACTIONS

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Kinetic investigations are concerned with at least two different aims:

1. The quantitative comparison of the properties of different objects (samples) under reproducible, defined conditions, regardless of the physical or chemical meanings of the kinetic parameters evaluated.

The progress here during recent years is obvious; computerization on a high mathematical level helps us to overcome difficulties and approximations, especially in the non-isothermal case, and it terminated the discussion on different kinetic methods during the 1970-s. In his contribution [1] and the introduction to the final discussion, Maciejewski once more pointed out the danger involved if we compare only one kinetic parameter (e.g. activation energy), without keeping in mind the others (e.g. frequency factor and reaction order).

However, these questions should be not the main subject of the final discussion of the topic in the title.

2. The attainment of a model description of the process under investigation, based on meaningful physical and chemical assumptions.

In this respect, we have to consider different sample characteristics, e.g. morphology and topotaxy [2], to check the experimental conditions [3], and to consider the real experimental conditions in a set of kinetic equations[4] and the specificity of the process as well as possible.

As concerns our own field of interest, the degradation of polymers, in certain cases we have to limit the degree of conversion to a few percent, not only because of the loss of essential properties in the practical use of the particular polymer, but also because of the unavoidable limitations due to secondary and side-reactions, which alter the compositions of the reaction products and/or the rate of the main reaction. For example, in the case of the degradation of polymers proceeding by random chain breaking and the subsequent formation of volatile reaction products without any change in the type of reaction, degradation products with different molecular masses may be formed, quite in contrast to low molecular weight

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inorganic or organic compounds, where the first and the last decomposing molecule, and also the reaction products, are of the same type.

In the case of the thermal degradation of PVC, investigated by TA, we tried to consider all the points mentioned above and to check a kinetic model (instead of one function $f(\alpha)$) under different isothermal and non-isothermal conditions [5]. In our opinion it is good evidence in favour of the proposed model if we get a good description of the process investigated under such different experimental conditions (heating rate 0.2–2.0 deg $\min^{-1}$, $T = 140$, 160 and 180° and the set of parameters seems not to be meaningless. At least we have "learned" from these investigations that the catalytic action of the reaction product (HCl) at the processing temperatures must be considered even in very thin sample layers (thin films or powders with small grain diameters.)

Finally, ESTAC 4 has also made it clear that numerous unsolved problems remain in the theory of solid-state reactions itself, even far from the problems of thermal analysis (e.g. [6]). To improve the situation, abundant experimental data are needed that are as accurate and as specific as possible, and the combination of thermal methods with other techniques, already widely used, is necessary. A special feature of kinetic investigations by thermal analysis seems to be *non-isothermal* reaction kinetics, the present situation of which is described in the outstanding contributions of Koch [7] and Šesták [8]. We have to agree with them that non-isothermal investigations have merits rather than disadvantages, and our task must be to accumulate such positive experiences.

References

1 M. Maciejewski, this Proceedings p. 243.

2 H. R. Oswald and A. Reller, this Proceedings p. 67.

3 G. Várhegyi et al., this Proceedings p. 87.

4 V. A. Logvinenko, ESTAC 4, Jena, 1987, plenary lecture PL 13.

5 J. Behnisch and H. Zimmermann, this Proceedings p. 191.

6 E. V. Boldyreva, ESTAC 4, Jena, 1987, final discussion.

7 E. Koch, this Proceedings p. 177.

8 J. Šesták, this Proceedings p. 1263.