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PROBLEMS OF KINETICS BY DTA

D. SCHULTZE

Zentralinstitut für Optik und Spektroskopie, Deutsche Akademie der Wissenschaften zu Berlin, Berlin-Adlershof, DDR

In the lectures of this symposium and in the literature too, there is a gap between good theoretical work, based on the assumption of idealized conditions, and good experimental work, with difficulties in the estimation of kinetic parameters. In DTA there are a number of theoretical models for kinetic interpretation of curves (theories of Borchard and Daniels, Kissinger, Piloyan or Reich), which, under certain conditions, may be used to determine kinetic parameters. The fulfilment of these conditions in practice is very difficult. The postulation of a low temperature gradient in the sample can hardly be satisfied in a dynamic regime as in DTA or DSC. The actual gas atmosphere around a sample cannot be controlled in many apparatuses. This actual gas atmosphere is greatly influenced by parameters such as particle size, geometry of sample holder and so on, which control gas diffusion. To put it polemically: From a DTA investigation of the decomposition of calcium carbonate in the open air one cannot calculate the kinetics of this decomposition, but perhaps those of gas diffiusion under special experimental conditions. This means that an accurate evaluation of a heterogeneous chemical reaction to obtain kinetic data is impossible by DTA without careful control of the actual gas atmosphere.

In the case of a homogeneous chemical reaction in a system in which no temperature gradient occurs (the basis of Borchard and Daniels' theory), the determination of kinetic parameters will surely be correct.

There are other problems concerning physical transformations in the solid state. In the investigation of a physical transition in a powder one gets the usual DTA diagram from which one can try to calculate kinetic data, for example on the basis of the theory of Borchard and Daniels. During the measurement, however, there is a thermal gradient throughout the sample. If we use a very small sample in a micro sample holder to minimize this gradient, we find a diagram with a number of small overlapping peaks. This is caused either by heat conduction phenomena or by a discontinuous phase change of single crystallites, mosaic blocks, domains or something similar, as was explained by Mazières. In the case of the ferroelectric–paraelectric transition at the Curie temperature the discontinuous phase change of single domains has been observed by hot-stage microscopy. The problem is which of the two diagrams – macro or micro sample – is the correct one from which to compute kinetic data.

It should be mentioned that in many cases there may be a great difference between "macro-kinetics", as measured integrally by thermal methods, and "micro-kinetics" of the same reaction, which can be described by the equations of chemical reaction kinetics. This difference is due to transport phenomena such as heat conduction or gas diffusion. I think that the gap between good theoretical work and the difficulty of obtaining accurate data even by careful experimental work is caused by the neglection of these differences between macro- and microkinetics.