

to realize that only this reduction on both coordinates is capable to visualize the actual error range of such measurements. It can be quite difficult to extrapolate back to the start of the reaction from the point where isothermal conditions are attained, etc.

In Fig. 6 the results of a series of runs with various preparations are shown as examples out of a larger collection of data. For comparison some of the functions of Table 5 are drawn out. We would also like to draw the attention to the fact that particle size distributions can change the shape of fractional decomposition curves considerably. It is often overlooked that this factor usually is much more important than the reaction mechanism itself. Gallagher⁸ has investigated the influence of a log normal distribution of spherical particles on a mechanism with one-dimensional diffusion. The broader the distribution, the faster is the starting period of the reaction

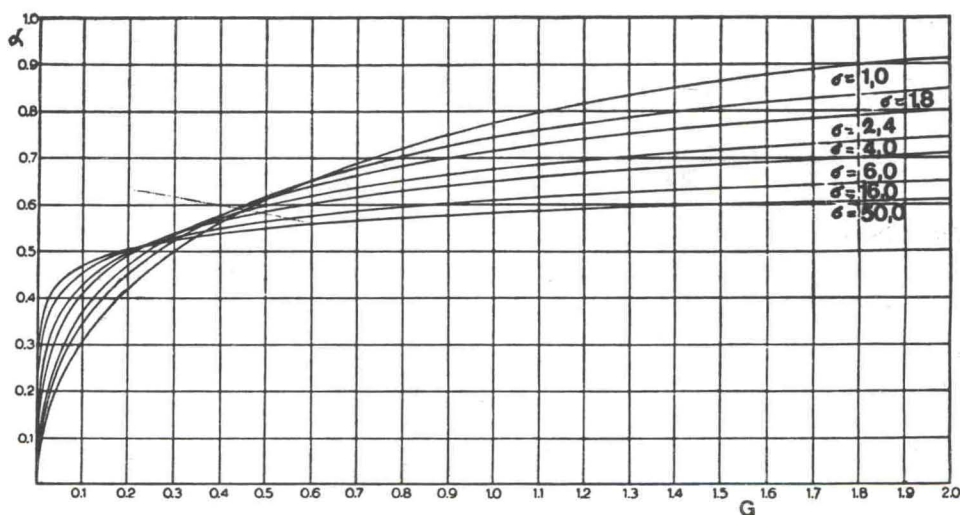


Fig. 7. Influence of particle size distribution on a particular reaction (D1)⁸.

up to 50%, and the more sluggishly ends the reaction. Figure 7 shows the fractional decomposition as a function of

$$G = \frac{\Pi^2 \cdot D \cdot t}{a^2}$$

where D is the diffusion coefficient, t the time, and a the geometrical mean of the sphere radius (from the volume distribution).

4. Unisothermal decomposition

Preliminary experiments with samples from 2 to 100 mg of preparation 1 showed the influence of the filling height in the crucible on the decomposition rate

(Fig. 8). Below a minimal and above a certain height the influence becomes less obvious. Within the range shown the decomposition again was apparently slower with larger samples than with small samples. This collides with x-ray evidence shown in Fig. 4.

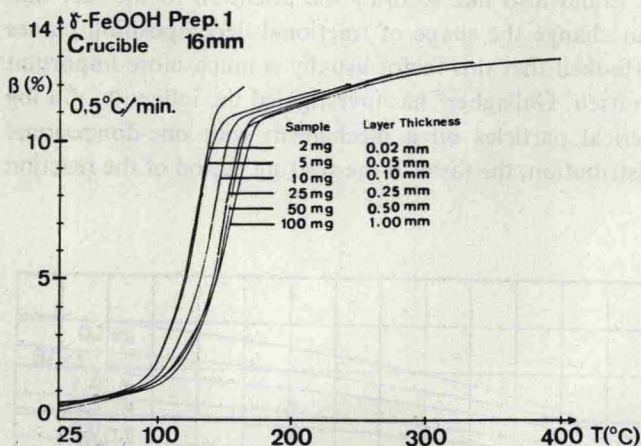


Fig. 8. Influence of filling height on decomposition of γ -FeOOH.

Unisothermal runs were undertaken in order to apply Šatava's method to determine the activation energy⁹ (see below). Figure 9 shows typical unisothermal decomposition curves. The form of such curves turned out to be heavily influenced by the heating rate. High heating rates expand the range of temperature within which the reaction is accomplished. This is undoubtedly an advantage for the subsequent evaluation. On the other hand the sample (a usually poor heat conductor) will at

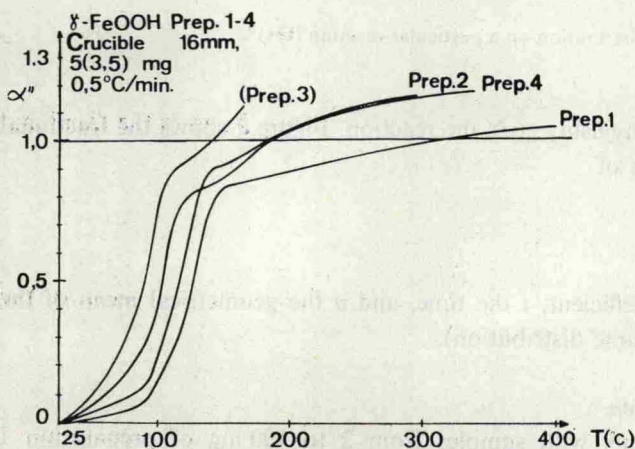


Fig. 9. Unisothermal dehydration of γ -FeOOH (sample curves).