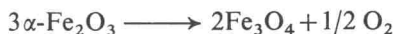


high heating rates no longer provide a smooth reaction. Under our conditions already a heating rate of $2^{\circ}\text{C min}^{-1}$ produces a non-uniform release of water which is most undesirable as the water vapour pressure within the sample then builds up to considerable values and influences the reaction. Therefore all isothermal experiments were done at the lowest possible rate of $0.5^{\circ}\text{C min}^{-1}$.

The four preparations, decomposed under identical conditions, may be compared here directly: The thermal stability decreases, as expected, with the specific surface. Up to about 80% decomposition all curves are very similar and only their location along the temperature axis varies. In other words the mechanism remains the same and only the pre-exponential factor is affected. The curves show, furthermore, that the weight loss due to dehydration approaches with increasing temperature more and more the region where the subsequent transformation to Fe_3O_4 under loss of oxygen begins. The three reactions



can thus not be clearly separated under the circumstances, nor is it possible to detect a plateau corresponding to desorption of physisorbed water before the dehydration starts.

5. Activation energy from isothermal data

In Fig. 10 the function $-\log d\alpha'/dt$ is plotted versus $1/T$, according to Wiedemann's method¹⁰. The slope yields the figures of Table 6. All activation energies are close to ≈ 29.5 kcal and deviations do not show any significant relation to the sample history nor to reactions conditions. The pre-exponential factor, however, is clearly

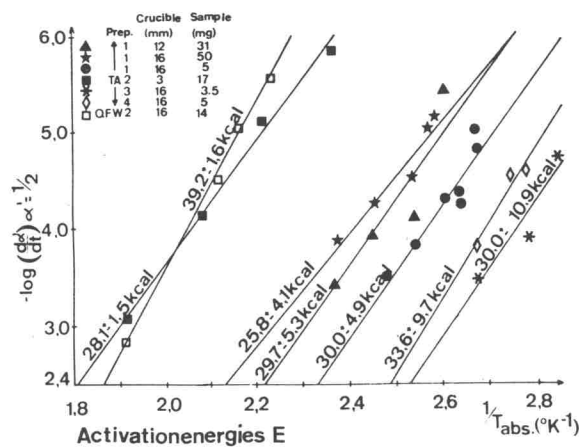


Fig. 10. Activation energies from various data collections.

TABLE 6
ACTIVATION ENERGIES FROM ISOTHERMAL DATA

Preparation No.	Crucible diameter (mm)	Sample (mg)	Activation energy (kcal mol ⁻¹)	Pre-exponential factor
1	12	31	29.7 ± 5.3	9.5 · 10 ¹¹
1	16	50	25.8 ± 4.1	4.1 · 10 ⁹
1	16	5	30.0 ± 4.9	7.0 · 10 ¹²
2	Microcrucible	17	28.1 ± 1.5	4.2 · 10 ⁸
3	16	3.5	30.0 ± 10.9	1.6 ± 10 ¹⁴
4	16	5	33.6 ± 9.7	8.1 · 10 ¹⁵

higher for the finely divided samples 3 and 4 as compared to 1 and 2. It might be added here that further experiments with higher filled crucible (higher sample thickness) produced lower pre-exponential factors.

6. Activation energies from unisothermal data

Šatava's⁹ method to determine graphically from unisothermal data the activation energy has the advantage that it takes into account the entire reaction while in methods using isothermal data the beginning of the reaction usually must be discarded as it will be part of the heating period. It has the grave disadvantage that the reaction mechanism must be known for proper evaluation*.

If we assume the time law D4 of Table 5 to be the best approximation for our reduced time isothermal data, and if we plot Šatava's function $\log g(\alpha)$ versus T , we get Fig. 11 and Table 7. In the latter the isothermally obtained data are included for comparison. The results are well within the experimental errors of the different methods and thus in satisfactory agreement.

7. X-ray diffraction

The following particle sizes of γ -Fe₂O₃, produced in the thermobalance in vacuo at 150°C (preparation 1) and in the furnace in vacuo at 200°C (preparation 3 and 4) were found (Table 8). All values are well within the limits of experimental error which has been estimated by Bartram¹¹ to be ± 1 Å (or $\pm 1\%$) for crystallite sizes around 82 Å but which, according to our own experience, is much higher. It should be noted here that the reflection 440 at $2\theta = 82^\circ$ (FeK_α) has been indexed 525 by Schrader¹².

According to Table 8 the γ -FeOOH crystals break into tiny, more or less equal crystallites, irrespective of the initial crystallite size. This is in accord with x-ray powder diffraction evidence (Fig. 12) although on the whole this seems to be highly suspicious for a reaction assumed to be topotactical.

*In Šatava's publication this is not a priori necessary. The application in our case showed, however, that it may be very difficult to operate without known formal time law.