SOME MACROKINETIC STRUCTURAL ASPECTS
OF HETEROGENEOUS THERMAL DISSOCIATION REACTIONS

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ABSTRACT

In order to determine the kinetic parameters with physical meaning, large series of coordination compounds with analogous structures must be studied.

Thermoanalytical methods for the investigation of thermal dissociation (based on the idealogy of non-isothermal kinetics) do not require large single crystals. It is enough to have a narrow fraction of grains (ideally single crystals, $d_{max}/d_{min} \leqslant 5$) and to determine experimentally the limits of the disappearance of the outer-diffusion hindrance (as a rule $d_{min} > 0.01$ cm). Such an approach allows one to study large series of coordination compounds with analogous structurates (changing the central atom, inner-sphere ligands or outer-sphere surroundings).

Attempts to correlate the structures of substances and the kinetic parameters of their thermal dissociations $(A_s \rightarrow B_s + C_g)$ are widespread in the literature, e.g., the relationship between the kinetic parameters and the degree of distortion of the coordination polyhedron.

Let us discuss two aspects of this general approach, which are usually neglected. This discussion will be based to a greater on the goals and problems of thermal analysis (and non-isothermal kinetics), than on the problems of solid-state chemistry. Let us keep in mind one-step reversible thermal dissociation reactions, such as dehydration or the elimination of a volatile ligand from the coordination sphere. These reactions usually start on the particle surface, then shift to the particle centre; the appropriate kinetic equation is that corresponding to a contracting sphere (in the limits of the transformation degree, $\alpha = 0.50$–0.60; otherwise the gas diffusion through the product layer must not be neglected).

It is known that the degree of overlap of orbitals is less on the crystal surface than in the crystal bulk, so that the interplanar spaces (lengths) in surface layers are more than in the bulk of the crystal ($> 11\%$ for a cubic

crystal with a face-centred lattice). This difference of 2% is maintained even in the fifth layer from the surface [1].

It is these distorted layers which are exposed to the decomposition; during their decomposition, more deeply located layers are affected by such distortion. Thus the kinetic parameters of the decomposition, as determined experimentally, correspond to this distorted structure with unknown symmetry, with unknown extent of distortion of the original coordination polyhedron. However, if we start with a series of compounds with well-known structures (e.g., with small increments in the distortion of the octahedron) it is possible that the distorted decomposing layers will have identical structures.

From this point of view, decomposition consists of two parallel reactions: thermal dissociation of distorted surface layers, and the transformation of the (structurally regular) layers next to distorted layers with elongation of interatomic bonds. In order to discuss this process in terms of transition-state theory (in any interpretation!), it is necessary to include both decomposing coordination spheres and transforming ones in the activated volume of the transition state [2].

It is reasonable that the physical boundaries of the distorted and undistorted (surface-bulk) crystal layers are diffuse, but this does not affect the meaning of the above-mentioned considerations. The kinetics of the thermal dissociation are determined by this complex process, and the experimentally observed wide range of the pre-exponential factor (for a series of related compounds) is due to the different degrees of involvement of these transforming coordination spheres. The involvement of deeper transforming layers of the crystal lattice in the chemical act of thermal decomposition is reminiscent of solvation in solutions, but whereas the solvent is one and the same for the whole series of compounds, the "surroundings" of a crystal lattice naturally change from one compound to another.

The second aspect is the features of thermal dissociation in a high vacuum. It is known that, in order to obtain kinetic parameters free from large errors, it is necessary to employ experimental conditions far enough removed from the equilibrium state, because of interference from the reverse reaction. However, if we try to precalculate the remaining pressure of a gaseous product from thermodynamic data, this residual pressure will not be very low for errors of $\sim 3\%$ in the activation energy.

Experimental data for dehydration $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O +$ 2 H_2O in a high vacuum are plotted in Fig. 1 [3]. These experimental results are reliable and very precise. A distinct gap is observed in the dependence in the pressure range $p_{H_2O} = 1-10^{-1}$ hPa, instead of the expected uniform dependence. This cannot be attributed to the variation of the contribution from the reverse reaction.

New results on the dehydration of $CuSO_4 \cdot 5H_2O$ are plotted in Figs. 2 and 3 [4]; the investigators used thermoanalytical mass spectroscopy with

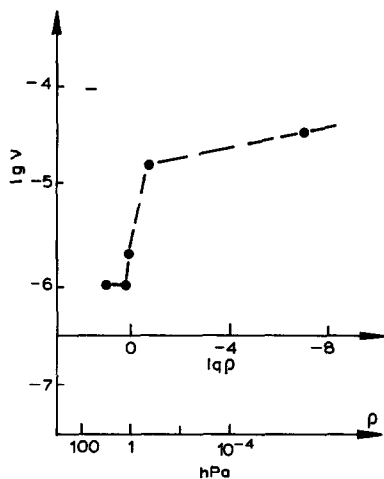Fig. 1. Dependence of the dehydration rate ($CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2\,H_2O$) on the water vapour pressure [3].

linear heating. The ion current curves represent the gas evolution (Fig. 2): the first peak is for the loss of two water molecules, the second peak is for a further two water molecules and the third peak is for the loss of the last water molecule. The peak areas are in accord with these assignments. The authors also studied the influence of storage of the pentahydrate sample in a vacuum ($P < 10^{-3}$ hPa) before heating (decomposition) on the features of the decomposition.

The results are plotted in Fig. 3. After keeping the sample in a vacuum for 100 min, the first peak corresponds to the loss of three water molecules and the second peak to the loss of one water molecule. This increase in the amount of water lost in the temperature interval corresponding to the first
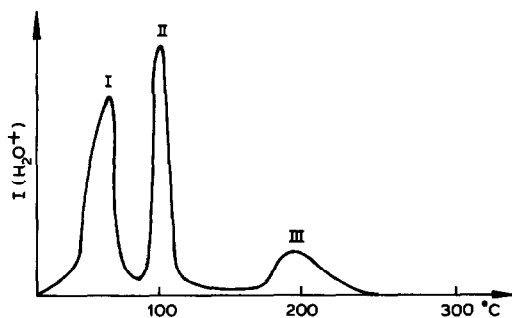

Fig. 2. Mass spectrum corresponding to the thermal dehydration of $CuSO_4 \cdot 5H_2O$ (three steps) in a vacuum [4]. (I) $CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O$; (II) $CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O$; (III) $CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O$.
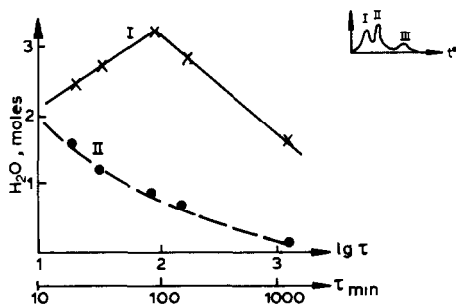
Fig. 3. The influence of storage in a vacuum upon the dehydration steps of $CuSO_4 \cdot 5H_2O$ [4].

peak (and the decrease in the amount in the temperature interval corresponding to the second peak) means that in a high vacuum the initial structure undergoes rearrangement before the dehydration process itself. It is quite possible for this rearrangement to proceed more rapidly than the dehydration reaction (as the sample decomposition is low in a vacuum in the absence of heating, and the sum of the water molecules corresponding to the first two peaks remains after 100 min of storage).

In some cases, if the experimental conditions result in little deviation from the equilibrium state, there will be one chemical reaction, one transition state and one (equilibrium) final product. On the other hand, if the experimental conditions result in a very large deviation from the equilibrium state in a high vacuum, there will be another starting compound, another chemical reaction, another transition state, another final product (may be a non-equilibrium one) and other kinetic parameters.

The marked change in the dehydration rate of $CuSO_4 \cdot 5H_2O$ with water pressure, P_{H_2O}, decreasing from 1 to 10^{-1} hPa (Fig. 1, ref. 3) may be explained by a change in the chemical reaction.

If the surface (already distorted) layers in a high vacuum are transformed into a novel structure before the thermal dissociation reaction itself, the kinetic parameters obtained will be incidental to the initial known structure of the crystal. In this case, experiments carried out not very far from the equilibrium state provide more relevant kinetic information about the reactivity of the original compound, though with some error because of the contribution of the reverse reaction.

Now we consider some contradictions in the kinetics of heterogeneous reactions, studied by thermoanalytical methods. Though we wish to study a chemical reaction of certain stoichiometry, a broad spectrum of various interplanar spaces topochemically takes part in the experimentally observed process, and it is not the original structure which is exposed to the decomposition process. One should expect noticeable anisotropy in the decomposition of different crystal faces, and therefore different kinetic parameters in different crystallographic directions. This is not very often observed.

The "monomolecularity" of most dehydration reactions in a high vacuum ($A = 10^{11} – 10^{14}$) indicates the possibility of drastic structural rearrangement of the crystal surface before the thermal dissociation itself, although it is generally accepted that there should be maximum deviation from the equilibrium state.

The limitations of the thermoanalytical approach to the investigation of heterogeneous topochemical macrokinetics arise from these contradictions. Thermoanalytical methods are oriented to the study of a sample, consisting of one or several particles—single crystals (1–10 mg). From the physicochemical viewpoint, this sample is taken to be representative of the compound studied. According to Aleskovskiy, the individual crystal is "a solid body" which forms part of the "solid chemical compound" [1]. The whole single crystal is regarded as a gigantic single macromolecule. In thermal analysis we are not concerned with the reactivity of isolated faces, model monomolecular layers, the elementary act of bond breaking, etc. One studies the transformation (during certain time and temperature intervals) of the crystal as a real individual "solid body", representative of the real "solid chemical compound".

Therefore the kinetic information obtainable for the thermal decomposition of a single substance is of little scientific importance; rather, a knowledge of the changes in these kinetic parameters over a series of substances is required when attempting to interpret the mechanism.

REFERENCES

1 V.B. Aleskovskiy, The Chemistry of Solid Compounds, Moscow, High School, 1978 (in Russian).
2 V.A. Logvinenko and G.V. Gavrilova, in F. Verzhbitskiy (Ed.), Thermal Analysis and Phase Equilibria, Perm, 1984, p. 3 (in Russian).
3 A.P. Chupahin, The Influence of the Water Vapour on the Kinetics of the Movement of the Reaction Boundary in the Dehydration of Crystal Hydrates, Thesis, Novosibirsk, 1983 (in Russian).
4 P.S. Korobejnikov and E.A. Obolenskaya, in Physico-Chemical Backgrounds of Rare-earth Raw Materials, Apatity, 1983, p. 111 (in Russian).