THERMAL DEHYDRATION OF INORGANIC SALTS IN WATER-SATURATED NITROGEN

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ABSTRACT

The thermal dehydrations of $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ have been investigated by TG, DTG and DTA in water-saturated nitrogen. The starting temperatures and the "activation energy" values for each step are reported.

INTRODUCTION

The development of thermoanalytical techniques and particularly the growing utilization of dynamic in respect of isothermal methods, has made possible a more accurate study of the thermal dehydrations of inorganic salts.

In the last years, the number of papers dealing with this subject has not decreased, since, to the analytical and inorganic interest, the need of a knowledge of the mechanism of solid-state reactions has grown.

From this point of view, the dehydration of inorganic salts is a convenient model owing to the great number of experimental data available and to the easy identification of the chemical process. The essentially physical nature of the processes at the solid state makes comparison of different experimental conditions particularly interesting.

In this work, we study the influence of the atmosphere on the dehydration of $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ by comparing experiments carried out in air and in water-saturated nitrogen.

EXPERIMENTAL

Materials
Reagent grade $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ were used.

Measurements
Simultaneous TG, DTG and DTA were carried out with a Mettler thermo-analyzer at a heating rate of $4°C \, min^{-1}$. A Mettler Model T-TD3 crucible holder, 0.3 ml Pt crucibles, and thermally inactive Al_2O_3 as reference material were used. For
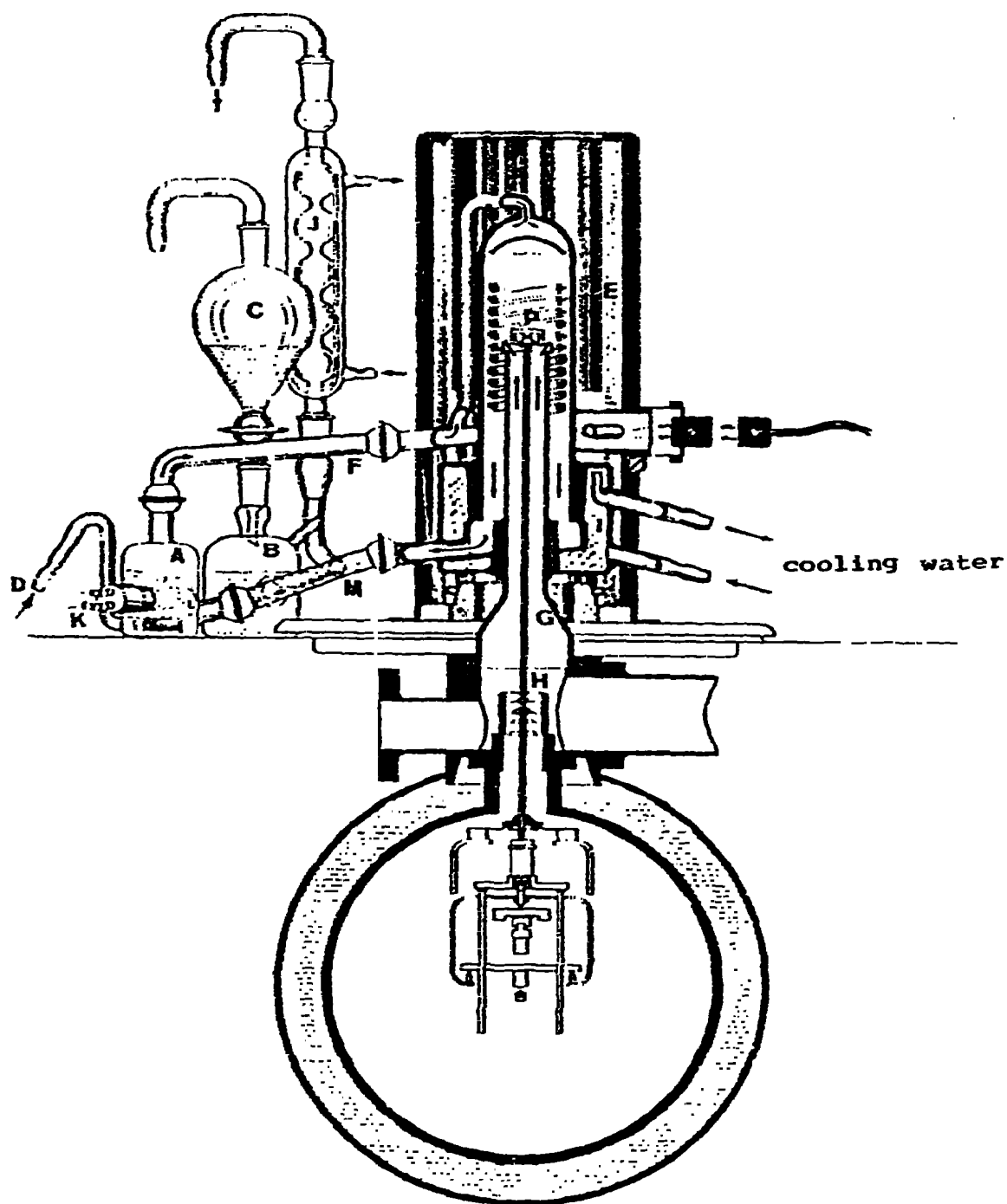
cooling water

Fig. 1. Scheme of the apparatus used for obtaining the water-saturated nitrogen atmosphere (from the book of instructions of the Mettler thermoanalyzer).

each salt, experiments were carried out in air and in water-saturated nitrogen. This latter atmosphere has been obtained by the apparatus shown in Fig. 1.

A flux of nitrogen (5 l h^{-1}) introduced into D, passes through the evaporator A where it is water saturated, and through pipe F it arrives in the furnace from where the condensed water goes back to A through pipe M.

The "activation energy" E_a^* values were calculated by the Piloyan method on DTA [1] and DTG [2] curves.

RESULTS AND DISCUSSION

From the thermoanalytical curves of $CoSO_4 \cdot 6H_2O$ in air and in water-saturated nitrogen (Fig. 2) we observe the following stoichiometry of dehydration:
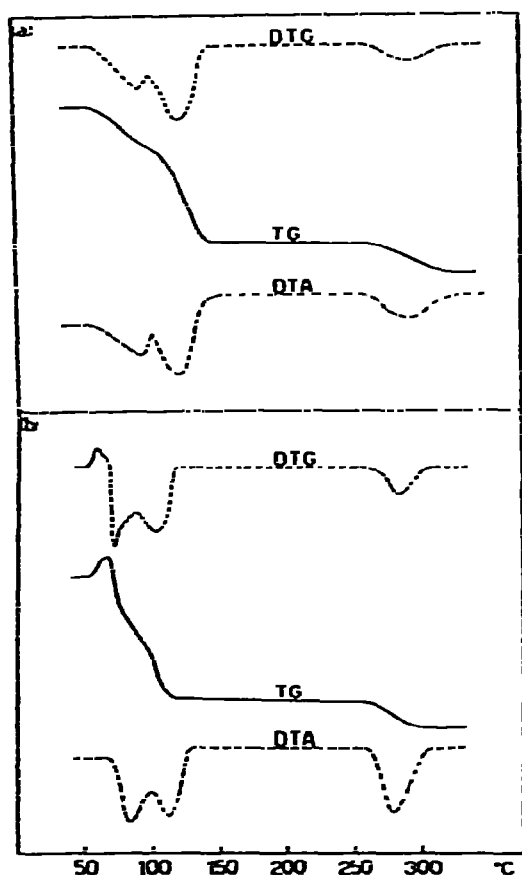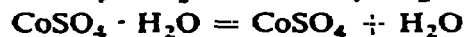
$CoSO_4 \cdot 6H_2O = CoSO_4 \cdot 4H_2O + 2H_2O$
$CoSO_4 \cdot 4H_2O = CoSO_4 \cdot H_2O + 3H_2O$
$CoSO_4 \cdot H_2O = CoSO_4 + H_2O$

Fig. 2. Thermoanalytical curves of $CoSO_4 \cdot 6H_2O$ at a heating rate of 4°C min^{-1}. (a) In air; (b) in water-saturated nitrogen.

The temporary weight increase observed before the beginning of the dehydration in the TG curve is present in all the experiments carried out in water-saturated nitrogen, and is due to an initial condensation of water on the sample, soon after it is released.

The first two steps of dehydration, in both experimental conditions under which we have operated, are not separated. The separation of these steps with a thermal range of stability of the tetrahydrate has been obtained by other authors[3] by adding before the experiment some $CoSO_4 \cdot 4H_2O$ (about 1%) to the sample of $CoSO_4 \cdot 6H_2O$. This suggests that in the first step the slowest process may be the nucleation of $CoSO_4 \cdot 4H_2O$.

In the third step, the observed weight loss, greater than about 6% of that corresponding to the stoichiometry of this reaction, can be explained by supposing an overlap of the end of the second step and the third step. This is confirmed considering that the thermogravimetric curve does not appear, before the third step, horizontal, indicating that the second reaction is not a simple one. On the contrary,
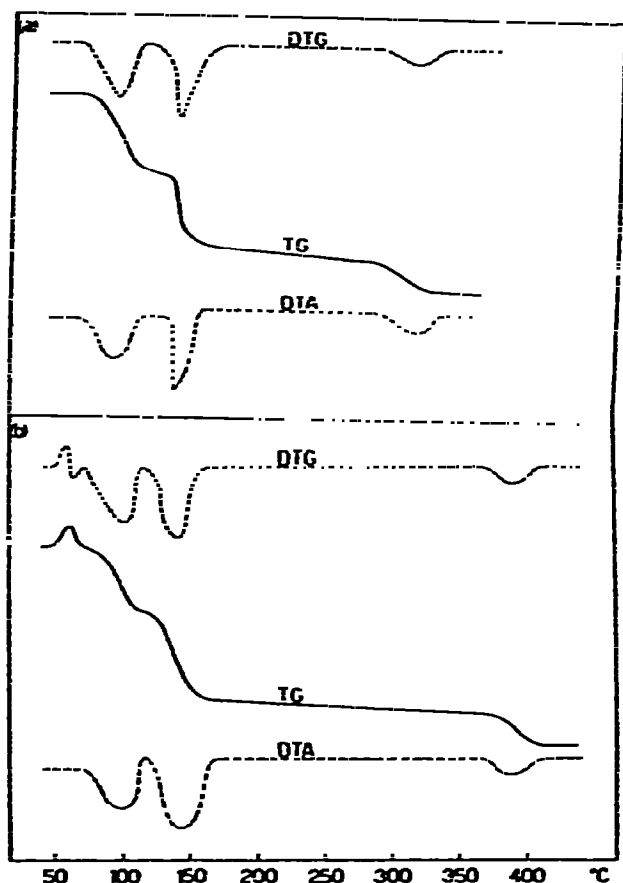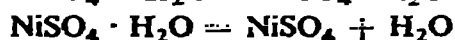

Fig. 3. Thermoanalytical curves of $NiSO_4 \cdot 6H_2O$ at a heating rate of 4 °C min^{-1}. (a) In air; (b) in water-saturated nitrogen.

the exhibition of two different kinetics, fast at the beginning, slow at the end, suggests the possibility of the formation of a very unstable intermediate product.

The thermoanalytical curves of $NiSO_4 \cdot 6H_2O$ are reported in Fig. 3. In this case, three different steps of dehydration can be identified, according to the following stoichiometry:

$$NiSO_4 \cdot 6H_2O = NiSO_4 \cdot 4H_2O + 2H_2O$$
$$NiSO_4 \cdot 4H_2O = NiSO_4 \cdot H_2O + 3H_2O$$
$$NiSO_4 \cdot H_2O = NiSO_4 + H_2O$$

The occurrence of an endothermic phase transition of $NiSO_4 \cdot 6H_2O$ has been reported[4], exhibited by DSC scan but not by a DTA curve. Also in our experiments no evidence of this transition has been found, so that the DTA peak observed during the first step of dehydration must be ascribed to the sum of two different thermal effects.

The existence of a range of thermal stability for $NiSO_4 \cdot 4H_2O$ and $NiSO_4 \cdot H_2O$ was already known[4-7]. From this point of view, no influence of the value of water vapor partial pressure is observed.
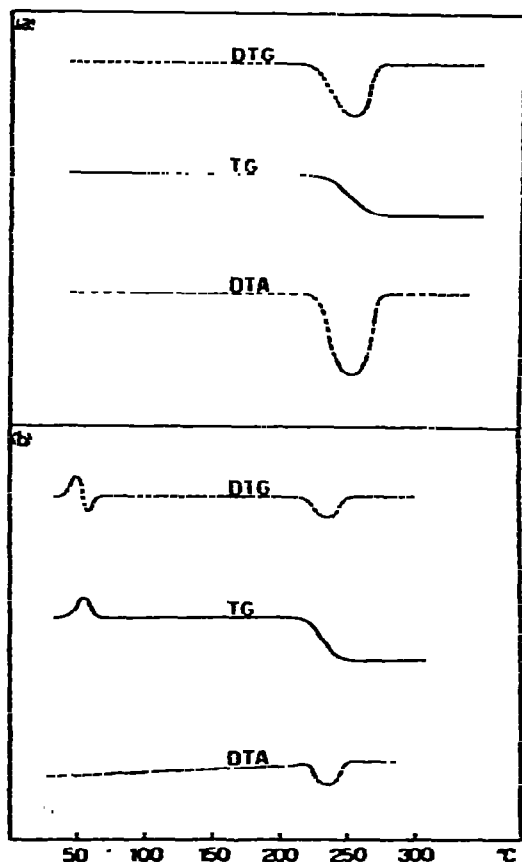

Fig. 4. Thermoanalytical curves of $MnSO_4 \cdot H_2O$ at a heating rate of 4°C min⁻¹. (a) In air; (b) in water-saturated nitrogen.

TABLE 1

STARTING TEMPERATURES T_i (°C) AND "ACTIVATION ENERGY" $E_a{}^*$ (kcal mol^{-1}) OF THE INVESTIGATED DEHYDRATION REACTIONS

Reactions	T_i		$E_a{}^*$			
	In air	In water- -satd. N_2	In air DTA	DTG	In water- -satd. N_2 DTA	DTG
$CoSO_4 \cdot 6H_2O \rightarrow CoSO_4 \cdot 4H_2O$	60	80	20	36	38	23
$CoSO_4 \cdot 4H_2O \rightarrow CoSO_4 \cdot H_2O$			13	17	8	9
$CoSO_4 \cdot H_2O \rightarrow CoSO_4$	260	275	38	42	22	15
$NiSO_4 \cdot 6H_2O \rightarrow NiSO_4 \cdot 4H_2O$	83	87	40	31	43	34
$NiSO_4 \cdot 4H_2O \rightarrow NiSO_4 \cdot H_2O$			98	97	43	43
$NiSO_4 \cdot H_2O \rightarrow NiSO_4$	310	360	10	25	22	46
$MnSO_4 \cdot H_2O \rightarrow MnSO_4$	224	226	16	67	55	53

In our investigation, together with polyhydrate salts, we have studied a mono-hydrate salt, $MnSO_4 \cdot H_2O$ (Fig. 4), whose existence also as pentahydrate is known. The interest in the study of this salt was to verify the possibility, under kinetically favourable conditions (high water vapor pressure and appropiately high temperature), of a hydration to a polyhydrate species. However, we have observed no hydration, since $MnSO_4 \cdot H_2O$ behaves as the other investigated salts, releasing soon the water before condensed, and the DTA curve exhibits no thermal effect before the dehydration of the salt to $MnSO_4$.

The starting temperatures and the "activation energy" values, calculated from DTA and DTG curves for each step of dehydration, are reported in Table 1.

As expected, the presence of a great water vapor partial pressure increases the starting temperatures. However, this effect, while it is sharply exhibited in some dehydration reactions, is slightly observable in other reactions.

Considering the kinetics, a first fact to point out is the difference between the values of E_a^* found for the same experiment, utilizing data from the DTG or DTA curve. This difference might be explained supposing that, together with dehydration, another process, chemical or physical, not strictly connected with weight loss, and associated with a significant thermal effect, occurs. This is also suggested by the case of the first step of dehydration of $NiSO_4 \cdot 6H_2O$, where we know, by DSC, the simultaneous occurrence of a phase transition.

The E_a^* values do not show a particular trend. Nevertheless, in the cases in which the values of E_a^* from DTA and DTG curves are almost the same, a faster kinetics in the experiments in water-saturated nitrogen is observed. Thus, the water desorption should not be a kinetically determining step of the investigated dehydrations.

The impossibility to draw general conclusions shows that also a theoretically simple reaction at the solid state, when the process is physically controlled, is actually the result of the simultaneous occurrence of many elemental processes, which are influenced by experimental conditions in a contradictory way.

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