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WATER–SOLID INTERACTIONS IN THERMAL ANALYSIS

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ABSTRACT

The effects of water on the thermal analysis of several salts and minerals and the thermal hydrolysis of hydrated salts are discussed. The discussion is based on contributions which were presented at the 8th ICTA Congress. The presence of water decreases the activation energies of various thermal reactions in the solid state. The following reactions were discussed: (1) thermal loss of zeolitic and structural water; (2) thermal hydrolysis of hydrated salts; (3) the contribution of water vapour to thermal crystallization and decomposition processes; (4) contribution of water to mechanochemical processes as determined by thermal analysis.

The presence of water has significant effects on various thermal reactions. Although the contribution of water to the mechanisms of the thermal reactions is still obscure, it is obvious that the presence of water decreases the activation energies of various reactions in the solid state [1]. Thermal analysis is useful for exemplifying some of the reactions, e.g., the papers by Šatava et al. [2,3] on differential hydrothermal analysis (DHA). The present communication summarizes six contributions that were presented at the 8th ICTA Congress which describe the effect of water on the thermal behaviour of several salts and minerals, and the thermal behaviour of hydrated salts.

These six papers represent different types of water–solid thermal reactions, and we have summarized them according to the type of water which is involved in the reaction.

A paper by Ulická and Žúrková [4] deals with the thermal properties of ammonium and potassium hydrogenhexavanadates. The hydrated salts, $NH_4HV_6O_{16} \cdot 3H_2O$ and $KHV_6O_{16} \cdot 3H_2O$, were investigated by DTA, DTG, XRD and IR spectroscopy. The water molecules may be considered as zeolite water, located with the ammonium or potassium cations between the

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polymeric vanadate chains. The ammonium salt lost most of its water along with some NH_3 within the temperature range 40–270 °C. Up to this stage the structure of the polymeric vanadate chains and the crystal structure of the salt were preserved. Complicated exothermic processes, which occurred at temperatures above 270 °C, involved a loss of ammonium and constitutional water, as well as the destruction of the vanadate chains and the formation of V_2O_5. The potassium salt lost most of its water within the temperature range 20–330 °C. Dehydration of zeolitic water did not have any effect on the crystal structure of the vanadate until 390 °C, when the vanadate chain lost constitutional water, decomposing into KVO_3 and V_2O_5. At this stage the original crystal structure of the potassium salt was destroyed. The final products of the decomposition of the original compound which crystallized from the melt obtained at 600–800 °C were $K_2V_8O_{20.8}$, $K_{0.27}V_2O_5$ and V_2O_5.

A paper by Shoval and Yariv [5] deals with the effect of alkali chlorides on the thermal hydrolysis of hydrated magnesium chloride, $MgCl_2 \cdot 6H_2O$. The six water molecules, which are part of the crystal structure of the salt, were coordinated to the magnesium (coordinated water). The inductive effect of Mg^{2+}, which has a small size and a high electric charge, led to thermal hydrolysis. In the first stage of the thermal treatment (up to 200 °C) $MgCl_2 \cdot 6H_2O$ lost five water molecules. The sixth water molecule reacted thermally in two stages:

(1) between 200 and 300 °C

$$Mg(OH_2)Cl_2 \rightarrow Mg(OH)Cl + HCl$$

(2) above 380 °C

$$Mg(OH)Cl \rightarrow MgO + HCl$$

DTA, TG and DTG of $MgCl_2 \cdot 6H_2O$ are shown in Fig. 1a. The three stages of the thermal treatment were accompanied by characteristic endothermic peaks. IR spectroscopy can be used to identify OH groups (~ 3600 cm^{-1}) and Mg–O groups (400–500 cm^{-1}). Figure 2a gives IR spectra of magnesium chloride heated to various temperatures. The spectra confirm that OH groups are developed at temperatures above 200 °C and decomposed at 400 °C. At the same time, MgO groups appeared.

Grinding $MgCl_2 \cdot 6H_2O$ with NaCl before the thermal treatment did not have any effect on the thermal behaviour of the magnesium salt; i.e., DTA and DTG curves similar to those of pure $MgCl_2 \cdot 6H_2O$ were recorded and the IR spectra showed the development and disappearance of OH groups at 200–300 and 400 °C, respectively, as well as the appearance of Mg–O groups (Figs. 1b and 2b).

When $MgCl_2 \cdot 6H_2O$ was ground with CsCl or KCl, solid solutions of the hydrated magnesium salt in the alkali halides were formed. The formation of the solid solutions resulted in DTA and TG curves which differed from the

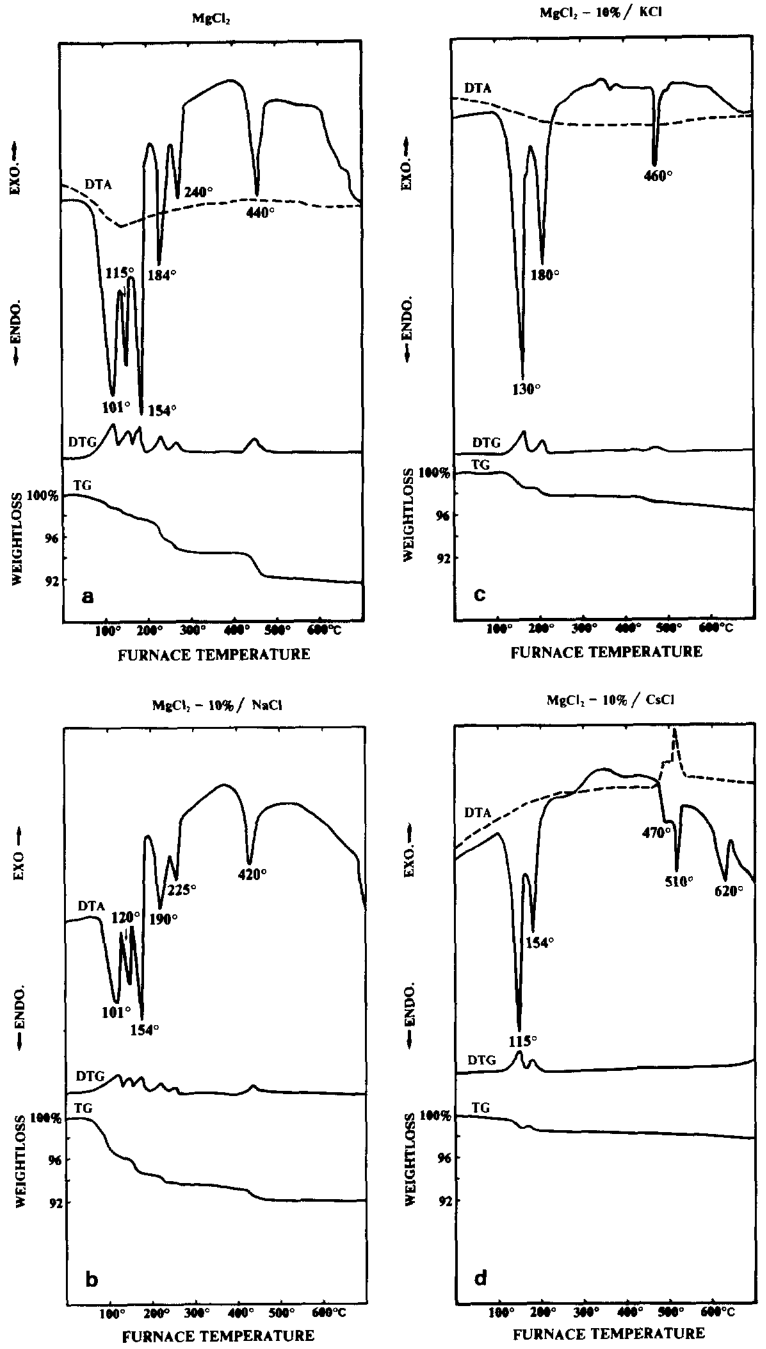

Fig. 1. DTA, TG and DTG curves of (a) pure $MgCl_2 \cdot 6H_2O$ and mixtures containing 10% $MgCl_2 \cdot 6H_2O$ and 90% alkali chlorides: (b) NaCl, (c) KCl and (d) CsCl. Temperatures given in the ordinate are those of the furnace. Temperatures assigned near the DTA peaks are those which were measured near the sample holder. (———) Heating curve; (– – – – –) cooling curve.

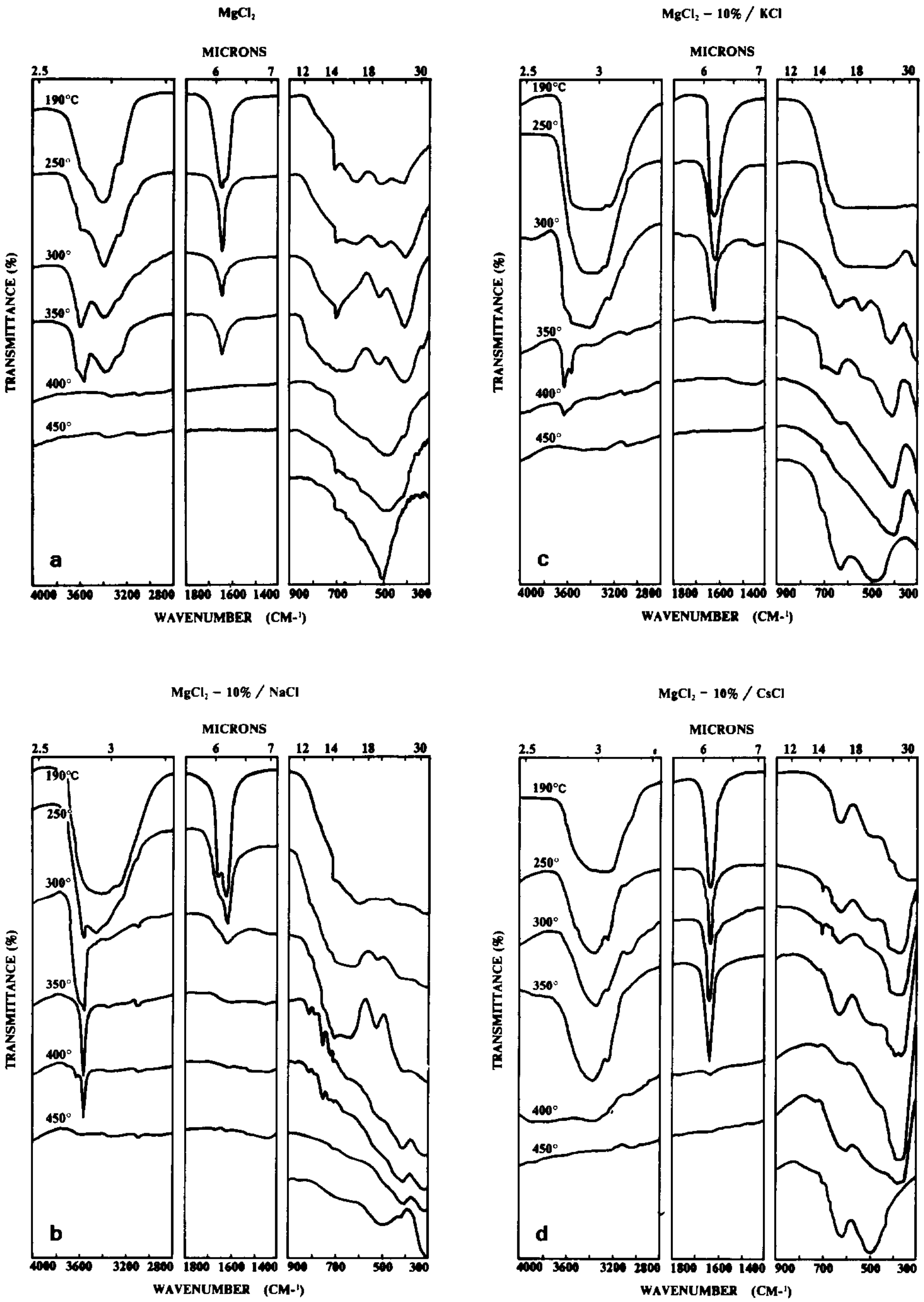

Fig. 2. IR spectra of $MgCl_2 \cdot 6H_2O$ thermally treated (a) as a pure powder and in disks containing 90% alkali chlorides: (b) NaCl, (c) KCl and (d) CsCl. First curve at 450°C, unground disk; second curve, disk reground three times.

curves obtained for pure $MgCl_2 \cdot 6H_2O$ (Figs. 1c and 1d). In the presence of CsCl the solid solution was very stable, avoiding the thermal hydrolysis of magnesium (Fig. 2d). The stability of the solid solution in KCl was lower and at 350°C hydroxyl groups were observed in the IR spectrum of the mixture (Fig. 2c).

The thermodynamics and kinetics of structural transformations of silica into quartz in a water vapour atmosphere were studied by Sharpataya et al. [6]. Normally, pure amorphous silica is an extremely stable compound. In air, under atmospheric pressure, it crystallizes only at temperatures above 1400–1500 K into cristobalite, but in the presence of alkali metal compounds the crystallization takes place at about 1100 K with the formation of quartz, tridymite or cristobalite. In a water vapour atmosphere silica is crystallized into quartz at temperatures of 620–820 K through several successive stages.

DSC was used for this study. Samples were located in sealed cells together with water and weak or strong crystallization activators (alkali salts). The effect of dehydration of the silica was observed between 340 and 700 K. In the presence of crystallization activators an exothermic effect was observed at 700–820 K which represented the crystallization of amorphous silica. This was followed by an endothermic effect at 853 K which represented the transition from α to β quartz.

Parallel experiments were carried out with an autoclave in order to study the crystallization kinetics. Samples of amorphous silica treated with a solution of a crystallization activator were kept with water for different times at certain temperatures. From the amount of quartz which was produced as a function of the reaction time, the activation energy of crystallization was calculated. It was found to be much lower than that of the high-temperature amorphous → cristobalite crystallization. This is probably due to the involvement of water vapour in the crystallization process.

Another paper which demonstrated the contribution of water vapour to a crystallization process was submitted by Garcia-Clavel et al. [7]. Normally, the high-temperature β polymorph of cadmium metavanadate is prepared by heating mixtures of different cadmium and vanadium compounds at temperatures between 650 and 800°C or by heating the low temperature α polymorph at 750–800°C. The authors succeeded in obtaining this polymorph in a practically pure state at 150°C from an equimolar $CdCO_3$–V_2O_5 mixture kept in a saturated atmosphere of water vapour for 24 h. When the mixture was left at 50°C, the α polymorph was obtained. The authors suggested that in the first stage water interacts with V_2O_5 and the crystalline vanadium oxide is transformed into a hydrated amorphous phase as follows:

$$V_2O_5(s) + H_2O(g) \rightarrow 2HVO_3(s)$$

In the second stage the amorphous hydrated vanadium oxide reacts with $CdCO_3$ as follows:

$$CdCO_3(s) + 2HVO_3(s) \rightarrow Cd(VO_3)_2(s) + CO_2(g) + H_2O(g)$$

A paper by Tkáčová et al. [8] deals with the changes in structure and enthalpy of magnesite on grinding in aerial and aqueous environments. Magnesite, $MgCO_3$, was ground in a laboratory vibration ball mill in an air atmosphere as well as in the presence of water for up to 8 h. Both grinding products were compared by measuring the heat of dissolution in HCl, X-ray diffraction lines and specific surface area as a function of grinding time. As one would expect, due to the lubricating effect of water, surface area measurements showed that smaller particles were obtained during grinding in air. On the other hand, the degree of crystallinity changed equally with time in both grinding systems. These results are surprising, since it is expected that the ground material will be somehow stabilized by surface adsorption of HOH molecules. The authors' interpretation of this phenomenon is that during grinding in the presence of air some of the material was aggregated. Aggregation protected the material to some extent from destruction; namely, it contributed some kind of stabilization of the system.

The thermal decomposition of magnesite and brucite was investigated by Hrabě and Svetík [9] using a thermobalance in a flowing atmosphere of air, H_2O, CO_2 and air/H_2O or H_2O/CO_2 mixtures. From the TG curves a temperature T_m was defined at which half of the decomposition reaction was completed. Activation energies were also calculated. The samples were then isothermally heated at 900°C for 45 min and the specific area was determined. The effect of the atmosphere on T_m and on the particle size was investigated. In the case of magnesite it is expected that a CO_2 atmosphere will lead to a higher T_m; indeed, T_m shifted from 857 to 935 K. In a water vapour atmosphere the opposite phenomenon was observed: T_m decreased to 779 K. There are two ways to explain this phenomenon.

(1) Molecular weight of the flow atmosphere. H_2O has a lower molecular weight than either O_2 or N_2 and in a constant gas flow the vapour is therefore lighter than air. The newly formed CO_2 molecules escape through the lighter H_2O system more readily than through the heavier air system.

(2) Surface reactions. The newly formed MgO crystals are stabilized by adsorption of H_2O onto the surface and the formation of surface OH groups.

In the case of brucite it is expected that in a flowing atmosphere of water vapour T_m will be located at a higher temperature; indeed, it shifted from 668 to 713 K.

In a flowing CO_2 atmosphere, T_m rose from 668 to 723 K. Let us examine this phenomenon in the light of the two explanations that were previously given for the effect of a flowing water vapour atmosphere on the decomposition of magnesite.

(1) Molecular weight of the flowing atmosphere. CO_2 is heavier than either air or water vapour. In a constant gas flow the pressure exerted by the flowing CO_2 atmosphere on the solid is higher than the pressure exerted either by flowing air or by flowing water vapour. Consequently the escape of newly

formed water molecules from the system is more difficult in the CO_2 atmosphere than in air or H_2O atmospheres.

(2) Surface reactions. Due to the high degree of symmetry of molecular CO_2, adsorption of CO_2 on the surfaces of MgO does not take place at these temperatures. In conclusion, a surface reaction between the flowing atmosphere and the solid thermal product cannot explain the increase in T_m. Explanation (1) should be used to explain the shift in T_m.

Let us examine the particle size of the thermal products of magnesite and brucite as obtained from surface area measurements (Table 2 of ref. 9). At the temperature T_m, very small particles of MgO were formed. Particle size increased with temperature. Crystal growth occurred mainly by the mechanism of recrystallization. Mg and O ions diffused from very small amorphous crystals to bigger crystals of a higher degree of order. Although at 900°C recrystallization has occurred to some extent, the present results can give information about the trend of crystal growth in the different flow atmospheres. Brucite thermal products show that there is no correlation between T_m and crystal size. On the other hand, the flow atmosphere has a great effect on the crystal size. In the presence of water vapour, very large particles of MgO were obtained either from magnesite or from brucite. This observation is in agreement with many geological observations of large crystals which were crystallized from hydrothermal environments.

REFERENCES

1 S. Yariv and H. Cross, Geochemistry of Colloid Systems, Springer Verlag, Berlin, 1979, Chap. 10, p. 401.
2 V. Šatava, O. Vepřek and D. Rykl, Thermochim. Acta, 10 (1974) 7.
3 V. Šatava, J. Am. Ceram. Soc., 58 (1975) 357.
4 L. Ulická and L. Žúrková, Thermochim. Acta, 92 (1985) 481.
5 S. Shoval and S. Yariv, Thermochim. Acta, 92 (1985) 819.
6 G.A. Sharpataya, G.P. Panasyuk, G.P. Budova, Z.P. Ozerova, I.L. Voroshilev and V.B. Lazarev, Thermochim. Acta, 93 (1985) 271.
7 M.E. Garcia-Clavel, S. Goñi-Elizalde and S. Fresno-Ruiz, Thermochim. Acta, 92 (1985) 501.
8 K. Tkáčová, N. Števulová, I. Hocmanova, H.P. Hennig, I. Ebert and H. Jost, Thermochim. Acta, 93 (1985) 713.
9 Z. Hrabě and S. Svetík, Thermochim. Acta, 92 (1985) 653.