

Interaction between MHSO_4 Salts ($\text{M}=\text{K}, \text{Rb}$) and Water Vapour

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The interaction between water vapour and salts of the MHSO_4 family depends not only on the vapour pressure and temperature but also on the sample history. E.g. a salt sample that has been cycled thermally several times tends to take up water more efficiently than a virgin sample. The amount of water that is taken up (n moles of water per mole of salt) depends on the water vapour pressure p . The gradient dn/dp changes drastically in a threshold region. Below this region dn/dp is small, but it is large above the threshold, where a slight increase in the vapour pressure tends to trigger a large uptake of water, and the initially homogeneous sample transfers gradually to a multiphase mixture. At 293 K this threshold is located in the vicinity of 14.5 torr for KHSO_4 (for samples that have not been cycled thermally) and somewhat higher for RbHSO_4 .

It is thus possible to obtain a non-congruent two-phase region which can be described as a solid phase $x\text{K}_2\text{SO}_4 \cdot y\text{H}_2\text{SO}_4$ and a liquid one $(1-x)\text{K}_2\text{SO}_4 \cdot (1-y)\text{H}_2\text{SO}_4 \cdot m\text{H}_2\text{O}$, where the final $m(\text{sat})$ is far above unity. The water vapour pressure is lower above such a noncongruent liquid than above a saturated salt solution, as obtained by dissolving KHSO_4 in pure water.

1. Introduction

Hydrogen bonds play an important role in several families of acid salts, such as MHAO_4 , $\text{M}_3\text{H}(\text{AO}_4)_2$ and $\text{MH}_3(\text{AO}_4)_2$, where $\text{M}=\text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ and $\text{A}=\text{S}, \text{Se}$, including systems with more than one alkali ion, e.g. $\text{Rb}_x\text{Cs}_{1-x}\text{HSO}_4$. There are similar families consisting of dihydrogen phosphates and arsenates. There are several reasons for the present interest in all these families of salts. Thus a large number of phases are ferroelectric, some high temperature phases are good proton conductors, proton glasses occur in some regions, etc. [1–4]. There is a considerable uncertainty concerning phases and phase transitions of these salts. Thus, while some phase transitions are well-established, others are considered to be “irreversible”, e.g. a transition that occurs when a sample is heated does not appear when the sample is cooled. We have demonstrated that the water vapour pressure above a sample can control phase transitions and phase stability in salts like CsHSO_4 and RbH_2PO_4 [5–7]. The purpose of the present investigation is to get a better understanding of the factors that are of importance for the interaction between acid salts and water vapour. Two more salts, KHSO_4 and RbHSO_4 ,

are studied. The very difference is that the weight changes are followed carefully during the uptake of water and the thermal cycling. In part, new ranges of water vapour pressure are covered. Additional work is in progress.

2. Experimental

We have been able to use a more accurate balance in the experiments reported here on the acid potassium and rubidium salts than we had when working with the cesium salt.

Solutions of the acid salts were prepared from stoichiometric amounts of sulphuric acid and either K_2SO_4 or Rb_2CO_3 . Crystals were obtained after slow evaporation of water. They were stored in a desiccator, and their weight was controlled regularly. In the isopiestic experiments well-defined water vapour pressures were obtained in small thermostated desiccators containing sulphuric acid of known concentration [6], and plastic beakers containing the samples were kept in them for a certain time. (The use of plastic beakers made it possible to observe the samples visually all the time.) All experiments were made at 293 K.

Two slightly different procedures were chosen. In most of the experiments with KHSO_4 the samples were taken out regularly for weighing. At the end of the exposure time a fraction of the sample was placed in our differential scanning calorimeter (DSC), where it was heated to at least 383 K. It was weighed after-

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wards, and it had usually gone back to the weight it had before any uptake of water. For the experiments with RbHSO_4 reported here, there were no intermediate weighings, but the exposure time was instead varied from about half an hour up to several weeks, using the same sample in a whole series. In this case each sample was thus exposed and cycled many times.

A few of the RbHSO_4 samples were also investigated thermogravimetrically (TG) from room temperature up to 403 K or 433 K.

3. Results and Discussion

The interpretation is complicated by the fact that there are quite a number of parameters that might influence the results of an individual experiment. Assuming that the temperature is kept constant, it is expected that the observed change in the sample's water content will depend on both the water vapour pressure and the exposure time. However, the sample mass can have an influence on the shape of the DSC trace, there can be considerable differences between a virgin sample and one that has been heated several times, and other details from the sample history can also be of importance.

Loss of water is considered to be the sole cause of the weight change. (Thermal decomposition of the acid sulphate to pyrosulphate has been found to occur for the cesium salt, but that was above 476 K [8, 9].)

The reported experiments on RbHSO_4 were performed before those on KHSO_4 , and the experience gained resulted in some modifications in the experimental procedure.

3.1. Potassium Hydrogen Sulphate

Virgin samples of KHSO_4 were used for all the experiments considered here. During the exposure to water vapour the samples were weighed at chosen time intervals, typically once or twice a day. The weight increased more slowly for a virgin sample than for one that had been cycled several times before. The weight increase will be given as n , the number of moles of water taken up per mole of salt. After some time the sample weight, and thus also n , fluctuated slightly within the accuracy limits of the weighing procedure. The experiments covered pressures from 11.8 torr and upwards. Both the final ratio $n(\text{sat})$ and the gradient $dn(\text{sat})/dp$ were correlated to the water vapour pres-

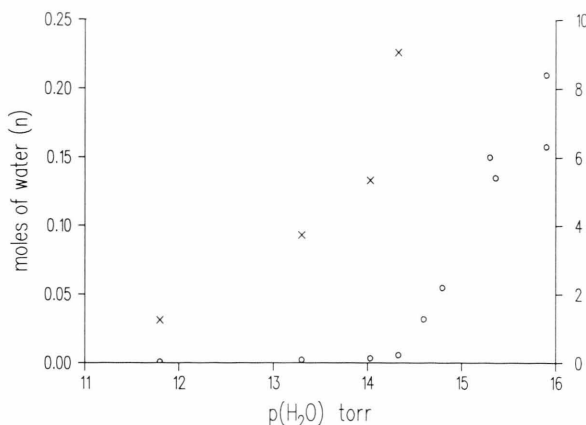


Fig. 1. Dependence of uptake of water on the water vapour pressure as found for KHSO_4 . n = moles of H_2O per mole of KHSO_4 . N.B. Two different scales for n , the one to the left is used for pressures up to 14.3 torr (\times) and the one to the right for the whole pressure range (\circ). The data above 14.5 torr are to be considered with some care, since they were taken before equilibrium had been reached, cf. text.

sure p . As long as this pressure was below a certain threshold, $n(\text{sat})$ was a rather small fraction of unity, e.g. of the order of 0.2 at 14.3 torr. In the threshold region, which was located around 14.5 torr (for samples that had not been cycled thermally), a minute increase in the water vapour pressure could cause a drastic increase in $n(\text{sat})$, see Figure 1.

The data taken above the threshold have to be considered with some care because the samples in question have to be kept in contact with water vapour for a very long time in order to reach equilibrium. It was noticed after some time that the crystals were "wet"; later on it was evident that two phases were present, namely crystals and a liquid. DSC analysis carried out on such samples gave evidence of a non-congruent state for the crystals and the coexisting liquid. It should be remembered that this happened for a smaller value of n than the one characteristic of a saturated solution of KHSO_4 , as obtained when the water-free salt is dissolved in pure water; in other words: the vapour pressure above our non-congruent solution is lower than above a saturated solution.

The described phenomena occurred at high water vapour pressures; the saturation pressure of water vapour is 17.54 torr at 20 °C.

In the above mentioned non-congruent region there is thus an equilibrium between a solid phase $x\text{K}_2\text{SO}_4 \cdot y\text{H}_2\text{SO}_4$ and a liquid one $(1-x)\text{K}_2\text{SO}_4 \cdot (1-y)\text{H}_2\text{SO}_4 \cdot m\text{H}_2\text{O}$, where the final $m(\text{sat})$ is far above unity.

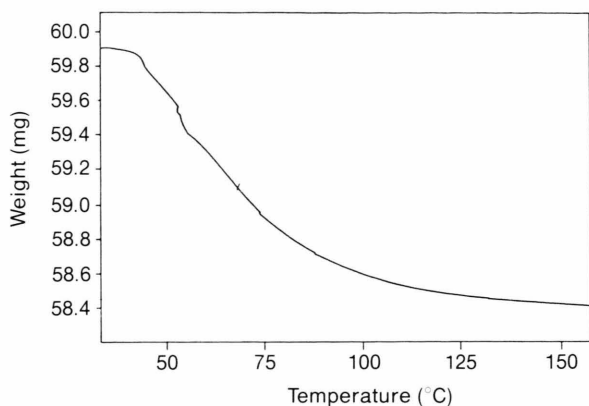


Fig. 2. Thermogravimetry study of a RbHSO_4 sample that has been exposed to a water vapour pressure of 13.4 torr for 1 hour. A fresh sample was used for this experiment. The accuracy of the temperature readings is uncertain.

Four different acid salts have been identified in the $\text{M}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ system for $\text{M}=\text{K}, \text{Rb}$ [10]. In the region with two condensed phases the non-congruent solid phase might correspond to a mixture of the acid compounds that have been identified in the literature.

As said above, a fresh sample was taken for each water vapour pressure, and each series of experiments was terminated by a DSC experiment. A detailed evaluation of the DSC will be presented on a later occasion; here it is sufficient to report that large and broad peaks were often found.

3.2. Rubidium Hydrogen Sulphate

Experiments with RbHSO_4 were performed in the vapour pressure range from 8.8 to 15.3 torr. As mentioned above, the experimental procedure was not exactly the same as for KHSO_4 . Now several experiments (ranging from only a few up to more than twenty) were made with the same sample at a chosen vapour pressure. As stated above, the rate of water uptake is considerably lower for a virgin sample than for one that has been cycled thermally. For this reason all our evaluations are based on data obtained with samples that had been cycled at least a couple of times before. For each series we estimated how long time it took before the water content of the sample in question was in equilibrium with that of the gas phase.

The same general tendency was found for RbHSO_4 as for KHSO_4 concerning the correlation of $n(\text{sat})$ with the water vapour pressure. We did not study the

highest vapour pressures as carefully for RbHSO_4 as for KHSO_4 , but it is obvious that also for RbHSO_4 there exist two regions corresponding to small and large values of dn/dp , respectively, cf. Figure 1. It is estimated that the high- dn/dp region lies at higher vapour pressures for the cycled samples of RbHSO_4 than for the virgin KHSO_4 samples. If virgin samples had been used also for RbHSO_4 , one should expect to obtain a somewhat larger distance between the two steep slopes.

About ten experiments were made at a vapour pressure of 8.8 torr. In all of them a slight uptake of water could be detected gravimetrically, but no peaks could be detected by DSC at this vapour pressure, while three out of the five experiments at 9.7 Torr gave a DSC peak; all three of them appeared at the same temperature, which of course might be fortuitous.

Five series of experiments (about 65 in total) were performed for vapour pressures between 10.9 and 14.1 torr. In contrast to the situation for lower as well as for higher vapour pressures there were tremendous variations within the individual series concerning the results. Most striking at first sight were the large differences regarding the temperature at which a peak was obtained and the variety in the shape of the DSC traces. It should be sufficient to report that there was a general trend that the uptake of water, n , increased when the vapour pressure was increased, and that for each individual experiment the measured peak enthalpy was lower than the energy that should be needed to remove the n moles of water that had been taken up in the same experiment.

A few thermogravimetry studies were performed on samples that had been exposed to a water vapour pressure of 13.4 mm Hg. The range up to 130 or 160 °C was covered. The total weight loss according to TG was in good agreement with what was obtained by weighing the sample before and after the TG. All the TG curves had a more or less pronounced S-shape, see Figure 2. The results should be taken as qualitative, since the temperature scale of the available TG device was not as accurate as that of our own DSC.

Two series of experiments (about 20 in total) were performed at 14.8 and 15.3 torr, respectively, i.e. in the region of the steep slope (cf. Fig. 1) beyond the pronounced change in the gradient dn/dp . In both series a phase transition was found at 357 ± 4 K. Since it is evident (from our experience obtained later on for KHSO_4) that equilibrium hardly could have been achieved for most of the experiments in question, one

must be cautious in the interpretation. However, besides the water uptake as well as the peak energy having been much higher than at the experiments discussed above, the enthalpies for the experiments at 15.3 torr were typically about two and a half times the heat of melting of pure RbHSO_4 , which is 22.4 kJ/mole at 476 K [11]. A straight-forward interpretation is that a considerable amount of water is vapourised in connection with some reconstruction of the solid part of the sample.

3.3. Comparisons with Some Other Investigations

There is reason to compare with some other recent studies of correlations between the water vapour pressure and the uptake or loss of water by solid ionic compounds. The impedus for that work is that a number of acid hydrates are known to have a pronounced protonic conductivity at ambient temperature [12], and correlations have been observed for such materials between the proton conductivity and water that is present in some form. Thus, for $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP), which is a "lattice hydrate", it has been found that the water content is quite constant for vapour pressures above 2.3 torr, while water is given off below that. ([12] gives relative humidities but not the temperature at which the study was done; we are here giving the corresponding vapour pressure at 293 K.) For the "particle hydrate" $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ there is a wide plateau at the stoichiometric composition $n=3$ where

an additional amount of surface water is adsorbed when the vapour pressure is increased. (This additionally adsorbed water is of great importance for the conductivity.) Vanadium pentoxide gels, $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, are "swelling hydrates", where a continuous and important swelling occurs for humidities above 14 torr, which may even lead to a colloidal solution.

Although both the vanadium pentoxide gels and our acid sulphates can transform into liquids at very high water vapour pressures, there is at least one important difference between the MHSO_4 salts and the mentioned types of hydrates, namely that the former are easily dissolved in water, giving ionic solutions, while the hydrates are either insoluble or give colloidal solutions. The hydrates in question are all examples of "wet" protonic conductors, while the high-temperature phases of many MHSO_4 salts are "dry" conductors [8].

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