Thermal and X-Ray Diffraction Studies of the System Sr(OH)$_2$—H$_2$O

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The system Sr(OH)$_2$—water has been studied by thermal and X-ray diffraction techniques in order to characterise the phases formed on heating Sr(OH)$_2$.8H$_2$O. Removal of water of crystallisation occurs in three steps, but only two of these appear to correspond to the formation of stable, crystalline phases. These are the mono-hydrate Sr(OH)$_2$.H$_2$O present at 140—150°C and the anhydrous hydroxide Sr(OH)$_2$ which is stable from 200°C to the melting point at 450°C. The present report lists enthalpies, densities, and unit-cell symmetries and dimensions for these phases.

1. INTRODUCTION

The system strontium hydroxide—water is of interest in connection with the electrodeposition of radioactive strontium isotopes for medical application. In a study conducted in 1967, a white deposit was obtained on platinum foil from a strontium solution in near anhydrous propyl alcohol. This deposit gave a complex X-ray powder pattern, unrecorded in the ASTM powder file for 1966. Chemical analysis indicated that strontium, oxygen, and hydrogen were the principal constituents of this material, but a definite composition could not be assigned. Heat treatment of commercial Sr(OH)$_2$.8H$_2$O, followed by X-ray analysis, demonstrated the formation of a second unidentified phase. On exposure to the atmosphere, this slowly gave way to the phase originally obtained in the electrodeposition study. The material obtained by heat treating the octahydrate had a density of 3.43 g cm$^{-3}$. After 20 h in the open, however, this figure had fallen to 3.02 g cm$^{-3}$ for a weight increase of a few per cent, corresponding to the formation of the electrodeposited phase.

In view of these results it was decided that an independent X-ray and thermal analytical investigation should be made into the decomposition of Sr(OH)$_2$.8H$_2$O in an effort to determine the nature and composition of these new phases.
2. EXPERIMENTAL

2.1. General. The approach chosen was to first study the decomposition of Sr(OH)$_2$.8H$_2$O using DTA, in order to distinguish the separate stages of the process. Thermogravimetry was then used to measure the change in composition occurring at each stage. Samples taken from the DTA crucible after heating to various temperatures were analysed by X-ray powder methods to determine the phase condition at each stage.

The above treatment was also applied to a sample of hydrate which, after being heated to 200°C, had stood in the open for 24 h.

2.2. Thermal analysis. Differential thermal analysis was performed on approximately 200 mg samples, contained in platinum crucibles. The samples were heated at a rate of 10°C min$^{-1}$ in an air stream of 151 h$^{-1}$. The Pt/Pt-10 % Rh thermocouples were calibrated against a benzoic acid standard melting at 122°C with a heat of fusion of 33.9 cal g$^{-1}$.

Thermogravimetry was conducted in platinum crucibles using roughly 100 mg of sample. In this instance, the heating rate was 5°C min$^{-1}$ in an air stream of 151 h$^{-1}$.

2.3. X-Ray analysis. Powder patterns of polycrystalline materials were recorded in a Guinier-Hägg focusing camera, using strictly monochromatic CuK$_\alpha$ radiation. A small quantity of silicon was mixed with each sample as an internal calibrant.

Measurements of the Guinier-Hägg powder patterns were used to derive accurate Bragg angles for the reflections of the various hydrate phases. The camera constant at points between the six Bragg angles defined by the silicon calibrant was computed, using a second degree Lagrange interpolation procedure. Unit cell dimensions were calculated from the values of $\sin^2\theta_{hkl}$ by the method of least squares, minimizing the function

$$R = \sum_{i=1}^{n} w_i (AQ_i)^2$$

where $AQ_i$ is the difference between the observed value of $4\sin^2\theta/\lambda^2$ for the $i$th reflection and the value calculated on the basis of the cell dimensions, and $w_i$ is a weight assigned on the basis of measurement reliability.

The reliability of results obtained in this way has been examined, using the criterion for no residual systematic errors given by the Likelihood Ratio Method. LRM calculations demonstrate that for the particular Guinier-Hägg cameras employed in this study, angle-dependent systematic errors in the $\theta$ data are less than the random errors in the measurement of $\theta$. Weights, $w_i$, were therefore calculated according to the scheme devised by Hess

$$w_i = 1/\sin^2 2\theta_i$$

on the basis of the precision in the measurement of $\theta$.

In these calculations, the wavelength of CuK$_\alpha$ radiation and the cell dimension of silicon at 23°C were assumed to be 1.54051 and 5.43062 Å, respectively.

On heating the octahydrate to a temperature above 450°C, a melt was obtained which on cooling could be crushed into fragments. One such fragment, coated with Canada balsam to prevent weathering, was mounted in a Weissenberg camera to obtain single-crystal patterns. Rotation-oscillation patterns and equi-inclination Weissenberg patterns for the first four layer lines were recorded with CuK radiation.

RESULTS

3.1. Thermal analysis

3.1.1. Thermogravimetry. Fig. 1. shows curves for the weight loss from two different samples of strontium hydroxide as a function of temperature.

Curve C1 represents the weight loss on heating Sr(OH)$_2$.8H$_2$O. The measured loss is 52 ± 1 %, as compared with 54.4 % calculated for the complete removal of water of crystallisation from ideally single-phase octahydrate. Differential
analysis of the curve affords three distinct temperatures, indicated in C1, at which changes occur following the onset of decomposition at 90°C. Two of these steps represent the formation of intermediates at 123°C (–2.5H₂O) and 145°C (–7H₂O), respectively. The third step corresponds to the formation of the ultimate decomposition product at 160°C (–8H₂O).

C2 is the weight loss for a sample after heating to 200°C and standing in the open for one day. The measured loss is 10 ± 1 % as compared with 12.9 % calculated for the elimination of one molecule of H₂O from Sr(OH)₂-8H₂O.

In C1, the evolution of the first seven water molecules occurs quite rapidly by comparison with that of the last molecule. In C2, where the starting material is Sr(OH)₂-8H₂O, the removal of the last water molecule occurs at an even slower rate.

3.1.2. DTA. Fig. 2 represents the thermal energy (enthalpy) of water evolution from Sr(OH)₂-8H₂O. The endothermal reaction C1 occurs in three decomposition steps, covering the temperature range of C1 in Fig. 1. The three peaks at 112°, 138°, and 150°C in the DTA curve evidently correspond to the three temperatures in the TG diagram, at which new phases are formed. The temperature differences are attributable to the higher rate of heating employed in the DTA run. The DTA curve C2 represents the decomposition of Sr(OH)₂-8H₂O; the starting material had the same origin as that used to obtain the TG curve C2 in Fig. 1.

Acta Chem. Scand. 25 (1971) No. 4
Fig. 2. DTA curves for thermal decomposition of 1, Sr(OH)$_2$.8H$_2$O; and 2, Sr(OH)$_2$.H$_2$O.

The quantitative evaluation of the DTA curves was made on the basis of the heat of fusion of benzoic acid, which yields calibration factors of 1.67 cal/mm$^2$ for C1, and 1.07 cal/mm$^2$ for C2. The measured enthalpies are accordingly 4220 cal for the decomposition

$$\text{Sr(OH)$_2$.8H$_2$O} \rightarrow \text{Sr(OH)$_2$} + 8\text{H}_2\text{O}$$

and 1560 cal for the decomposition

$$\text{Sr(OH)$_2$.H$_2$O} \rightarrow \text{Sr(OH)$_2$} + \text{H}_2\text{O}$$

These values are 2% higher than the enthalpy calculated for the complete dehydration of octahydrate, and 1.8% lower than that calculated for the dehydration of monohydrate.

3.2. X-Ray phase analysis of products of thermal decomposition

In addition to the starting material and small amounts of SrCO$_3$, two additional phases can be distinguished in the decomposition products formed on heating Sr(OH)$_2$.8H$_2$O in the DTA apparatus. These additional phases designated "X" and "Y" give complex powder patterns with more than 50 reflections each in the angular range up to 40° (θ). In neither case is the powder pattern recorded in the ASTM Powder Diffraction File for 1966.

_Acta Chem. Scand._ 25 (1971) No. 4
The balance of the above phases, as they occur in samples taken from the DTA crucible at temperatures between 105 and 180°C, is given in Table 1.

**Table 1. Phase analysis of products formed in thermal decomposition of Sr(OH)$_2$·8H$_2$O.**

<table>
<thead>
<tr>
<th>X-Ray No.</th>
<th>Thermal treatment</th>
<th>Phases present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI 6</td>
<td>Sr(OH)$_2$·8H$_2$O heated to 105°C in DTA apparatus and cooled</td>
<td>Sr(OH)$_2$·8H$_2$O “X”</td>
<td>Octahydrate and “X” phase present with octahydrate reflections dominant.</td>
</tr>
<tr>
<td>AI 1</td>
<td>As above, cooled from 130°C</td>
<td>Sr(OH)$_2$·8H$_2$O “X” SrCO$_3$</td>
<td>Octahydrate and “X” phase present in roughly equimolecular amounts. SrCO$_3$ represented by 4–5 weak reflections. Patterns of “X” and SrCO$_3$ ill-defined, characteristic of poor crystallinity.</td>
</tr>
<tr>
<td>AI 2</td>
<td>As above, cooled from 140°C</td>
<td>“X” SrCO$_3$ Sr(OH)$_2$·8H$_2$O</td>
<td>“X” is dominant phase, SrCO$_3$ at estimated 5 mol% level. Octahydrate at trace (~1 mol%) level. Pattern of “X” phase sharper than in AI 1.</td>
</tr>
<tr>
<td>AI 4</td>
<td>As above, cooled from 150°C</td>
<td>“X” SrCO$_3$</td>
<td>Clear, sharp pattern of “X” up to θ max (45°). SrCO$_3$ still at ~5 mol% level. No trace of octahydrate.</td>
</tr>
<tr>
<td>AI 3</td>
<td>As above, cooled from 160°C</td>
<td>“X” SrCO$_3$ “Y”</td>
<td>“X” is still dominant phase with SrCO$_3$ at ~5 mol% level. New phase “Y” is represented by three reflections. Pattern of “X” is again diffuse indicative of decreased crystalline perfection as compared to condition in AI 4.</td>
</tr>
<tr>
<td>AG 2</td>
<td>As above, cooled from 180°C</td>
<td>“Y” SrCO$_3$</td>
<td>Clear, sharp pattern of “Y” up to θ max (45°). SrCO$_3$ retains same strength. No trace of “X” phase. The pattern is identical for samples heated at temperatures from 200°C to the melting point (~450°C).</td>
</tr>
<tr>
<td>AH 12</td>
<td>Octahydrate heated to 200°C, cooled and left in the open for 48 h</td>
<td>“X” SrCO$_3$</td>
<td>Slightly diffuse pattern of “X”. SrCO$_3$ at estimated 10 mol% level. No trace of “Y” remains.</td>
</tr>
</tbody>
</table>

From the results of the thermal analysis described in 3.1, phase “X” is recognised as having the composition Sr(OH)$_2$·H$_2$O, and “Y” is identified as anhydrous strontium hydroxide Sr(OH)$_2$. It has not been possible, however, to detect in the powder patterns reflections corresponding to the phase intermediate between Sr(OH)$_2$·8H$_2$O and Sr(OH)$_2$·H$_2$O expected from the results of thermal analysis.

On standing in the open, rehydration of Sr(OH)$_2$ to the monohydrate occurs, as is shown by powder pattern AH 12. Although the pattern is not ideally sharp, the monohydrate reconstituted under these conditions is surprisingly well crystallised, considering its room temperature formation.

*Acta Chem. Scand. 25 (1971) No. 4*
Table 2. Crystallographic data for the strontium hydroxides.

<table>
<thead>
<tr>
<th>Phase composition</th>
<th>Symmetry</th>
<th>Space group</th>
<th>Cell dimensions in Å</th>
<th>Density in g cm⁻³</th>
<th>Film No.</th>
<th>No. of sin²θ used in refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(OH)₂·8H₂O</td>
<td>Tetragonal</td>
<td>P4/ncc</td>
<td>a₂ 9.0163 ± 2, c₂ 11.6078 ± 4</td>
<td>1.88₂, 1.870</td>
<td>R 10</td>
<td>69</td>
</tr>
<tr>
<td>Sr(OH)₂·H₂O</td>
<td>Orthorhombic</td>
<td>Pnma or Pm2a</td>
<td>a₂ 6.7147 ± 2, b₂ 3.6482 ± 1, c₂ 6.1992 ± 2</td>
<td>3.02₂, 3.054</td>
<td>AI 4</td>
<td>63</td>
</tr>
<tr>
<td>Sr(OH)₂</td>
<td>Orthorhombic</td>
<td>Pnma (PbCl₂-type)</td>
<td>a₂ 9.8889 ± 5, b₂ 3.9187 ± 2, c₂ 6.1175 ± 2</td>
<td>3.42₂, 3.408</td>
<td>AG 2</td>
<td>76</td>
</tr>
</tbody>
</table>

3.3. Unit cells and space group symmetries of the strontium hydroxides

3.3.1. Sr(OH)₂·8H₂O. The crystal structure of the octahydrate is well established from single crystal studies. The unit cell is tetragonal with the space group symmetry P4/ncc. The powder pattern obtained in this investigation affords unit cell dimensions (Table 2) with an accuracy appreciably greater than that given in the literature. Powder pattern data are listed in Table 3.

3.3.2. Sr(OH)₂·H₂O (phase X). The powder pattern of this phase was indexed unambiguously with the programme INDEXT using the twenty-eight reflections in the low-angle (sin²θ ≤ 0.3) region as input. The proposed unit cell is orthorhombic, and the only condition limiting possible reflections is h = 2n for hkl. Thus in the angular region, sin²θ ≤ 0.48, six of the nine reflections permitted by this condition are visible, while the nine hkl reflections with h = 2n + 1 are absent. The probable space group symmetry is accordingly Pnma, or its non-centric congener Pm2a.

The cell dimensions in Table 2 have been obtained from the well-crystallised material (X-ray No. A14), referred to in Table 1. Good agreement is obtained between the observed density and the density calculated on the basis of these dimensions and a unit cell content of 2[Sr(OH)₂·H₂O]. Powder pattern data are listed in Table 4.

3.3.3. Sr(OH)₂ (phase Y). It was established in 3.1, that anhydrous strontium hydroxide is obtained on heating the octahydrate to 200°C. X-Ray powder patterns demonstrated that this phase was formed on cooling from the melt at 450°C. Since the crystal structure of this compound is not described in the literature, it was decided to determine the symmetry from a single crystal study.

An acicular fragment, roughly 50 μ in diameter, was mounted with the needle axis as rotation axis in a Weissenberg camera. Single crystal patterns demonstrated that the fragment had orthorhombic symmetry and the approximate unit cell dimensions.
The rotation axis corresponded to the b axis of the crystal.

Systematic absences in the layer lines 0 ≤ k ≤ 3 were observed to occur for h = 2n + 1 in hko -- and k + l = 2n + 1 in okl-type reflections. These conditions correspond to the requirements for the centrosymmetric space group Pnma and the non-centric alternative Pn2a. Comparison of the layer line patterns


The parameter a₀ = 9.89, b₀ = 3.95, c₀ = 6.17 Å.
shows, however, that the intensity distribution for $h0l$-type reflections is closely similar to that for $h2l$ reflections. A similar correspondence is seen to apply for layer lines $h1l$ and $h3l$. The constituent Sr and O atoms are accordingly confined to layers extending normal to the $b$ axis with a separation of $b/2$.

An arrangement of the above type can only be accommodated by the centric space group $Pnma$, with all atoms placed in $4(c)$ positions, for which the $y$ coordinates are fixed at $\pm 1/4$. This, together with the unit cell dimensions, strongly suggests that Sr(OH)$_4$ has the PbCl$_4$-type crystal structure with a unit-cell content of four molecules.

The cell dimensions of Sr(OH)$_4$ (Table 2) were refined, using data collected from the powder patterns of material heated to 180°C. The observed density is seen to be in good agreement with the density calculated on the basis of these dimensions and a unit cell content of 4[Sr(OH)$_4$]. The powder data are listed in Table 5.

Table 5.

<table>
<thead>
<tr>
<th>REFINEMENT OF</th>
<th>Sr(OH)$_4$</th>
<th>ORTHORHOMBIC</th>
<th>Pnma</th>
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<tr>
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<tr>
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<td>0.256848</td>
<td>0.0000018</td>
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</table>

NUMER OF REFLECTIONS = 76

4. DISCUSSION

The system strontium hydroxide-water comprises three thermally stable crystalline phases, namely strontium hydroxide octahydrate Sr(OH)$_2$.8H$_2$O, the monohydrate Sr(OH)$_2$.H$_2$O, and the anhydrous hydroxide Sr(OH)$_2$. Thermal decomposition of the octahydrate to the anhydride commences at 90°C, and occurs in three steps with DTA indications at 110—112°C, 132—138°C, and 150—160°C. Dehydration is complete at 200°C.

X-Ray phase analysis demonstrates that the anhydride begins to form at 160°C. Similarly, the presence of monohydrate can already be detected in the

Acta Chem. Scand. 25 (1971) No. 4
sample cooled from 105°C. There is no X-ray evidence for the formation of a phase intermediate between the octa and mono hydrates. In view of the occurrence of mixtures of these two phases between 105° and 140°, the formation under equilibrium conditions of an intermediate phase is forbidden by the phase rule, assuming the system to be truly binary in character. It is therefore suggested that the step between 90° and 112°C, observed in both the DTA and TG studies, represents a kinetic effect, possibly associated with the creation of a transient condition in the decomposing octahydrate crystals.

Monohydrate formed at 140—150°C begins to lose its crystallinity at 160°C and is completely decomposed at 180—200°C. It can readily be reconstituted from the anhydrous hydroxide, however, on exposure to atmospheric moisture at room temperature. Continued exposure does not lead to the reconstitution of the octahydrate.

Strontium hydroxide crystallises with an orthorhombic structure resembling that of PbCl₂. The only other hydroxide reported as having this structure is Pb(OH)₂. The majority of the remaining dihydroxides, including Mg(OH)₂ and Ca(OH)₂, crystallise with the simple layer-like trigonal structure of CdI₂. The exceptions are Be(OH)₂ and Zn(OH)₂, which have orthorhombic unit cells and constitute a third structural group.

The transition from the CdI₂-type structure in Mg(OH)₂ and Ca(OH)₂ to the PbCl₂-type configuration in Sr(OH)₂ is probably induced by conditions of atomic packing. Thus the M²⁺ ions in the CdI₂-type hydroxides have radii less than 1 Å, whereas the ionic radii of Sr²⁺ and Pb²⁺ are 1.12 and 1.20 Å, respectively. It is accordingly to be expected that since r_{Ba²⁺} = 1.34 Å, Ba(OH)₂ will also crystallise with the PbCl₂-type structure.

The structure of Sr(OH)₂·H₂O appears to be unique, no other compound having been reported as crystallising with this configuration. The unit cell is clearly derived from that of Sr(OH)₂, as can be seen by inspection of the cell dimensions and symmetries given in Table 2. Thus the b₀ and c₀ dimensions of the unit cells are fairly similar, being changed only slightly by the addition or removal of water of crystallisation. Even more striking is the retention of the symmetry elements in the [010] and [001] directions, with changing water content. The main structural alternation is in the [100] direction. For comparison purposes, a structure cell of Sr(OH)₂·H₂O may be chosen with a₀ = 2 a₀, so that, as with the anhydrate, a cell is obtained which contains four molecules. On losing the 4H₂O water of crystallisation, the a₀ dimension of the monohydrate cell is now seen to decrease from 13.43 to 9.89 Å. This corresponds to a density increase from 3.03 in the monohydrate to 3.42 g cm⁻³ in the anhydrate for an overall loss in weight, calculated to be 13 %.

The close structural relationship which, on the basis of the above similarities, seems to exist between Sr(OH)₂ and Sr(OH)₂·H₂O is probably responsible for the ease with which the monohydrate can be reconstituted in a well crystallised condition at room temperature on exposing the anhydrate to atmospheric moisture. Knowledge of the atomic arrangements in these two compounds would permit a more detailed description of the geometrical changes underlying this process.

Similar results to those described here have been obtained for the system Ba(OH)₂—H₂O. These will be reported later.

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