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THERMAL DECOMPOSITION OF STRONTIUM HYDROXIDE

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The thermal behaviour of strontium hydroxide octahydrate was studied by thermal analysis, an X-ray diffraction technique and optical microscopy. Up to 210° this compound transforms to the hexahydrate and then to the monohydrate. Anhydrous strontium hydroxide crystallizes in the tetragonal system and a polymorphous transformation may occur at 480°. From 530° on it decomposes in three stages. Amorphous strontium oxide is obtained at 700°.

When ceramic bodies containing free strontium oxide are hydrated, strontium hydroxide results, and this causes their deterioration.

According to literature data two strontium hydroxide compounds exist in the hydrated state: the octahydrate and the monohydrate.

Strontium hydroxide octahydrate – $Sr(OH)_2 \cdot 8\,H_2O$ – may be obtained by crystallization from an aqueous strontium hydroxide solution [1], or by precipitating strontium hydroxide from the nitrate with NaOH and washing the precipitate with cold ethyl alcohol [2]. It crystallizes in the tetragonal system with the unit cell constants $a = 9$ Å and $c = 11.58$ Å [3], or $a = 6.422$ Å and $c = 5.281$ Å [4].

From a study of the solubility of $Sr(OH)_2$ in water, Latimer [5] has shown that the octahydrate becomes metastable at a temperature of 80°.

The existence of strontium hydroxide monohydrate – $Sr(OH)_2 \cdot H_2O$ – is reported by Reinders and Klinkenberg [6], who consider that it is formed in solution at 87.7°. The monohydrate was also obtained by drying the octahydrate in vacuum or in a current of hydrogen at 45–50° [7].

Anhydrous strontium hydroxide may be obtained by heating the octahydrate for 15 minutes at 320° [2]. Similarly, the monohydrate loses the last water molecule at about 100° to form anhydrous strontium hydroxide [1].

Anhydrous strontium hydroxide starts to lose water at around 540°, but has to be heated to 800° to yield anhydrous strontium oxide [1, 8].

The unreliable data concerning the thermal changes of strontium hydroxide octahydrate point to the need of further work.

Experimental

1. *Preparation of the compounds.* The starting substance was strontium oxide obtained by calcination of reagent grade "Reactivul" strontium carbonate at 1400°.

Strontium hydroxide octahydrate was obtained by dissolving strontium oxide in carbon dioxide-free distilled water, and by crystallization from the solution. The product was dried at 80°. The sample was placed in a crystallizer maintained carbon dioxide-free, with anhydrous calcium chloride and sodium hydroxide.

The monohydrate was obtained by drying the octahydrate at 150° in a carbon dioxide-free atmosphere.

Anhydrous strontium hydroxide was obtained by drying the octahydrate at 200° in a carbon dioxide-free atmosphere.

2. *Methods of determination.* The octahydrate was studied using a Paulik–Paulik–Erdey Derivatograph OD-102. The samples were tested in Pt crucibles.

The temperatures on the DTG curve were increased by 10° to bring them into agreement with those on the DTA curve.

The microscopic analysis was carried out with an MC-1 IOR microscope.

The phase analysis was performed roentgenographically by the Debye-Scherrer method with Cu Kα radiation on a TUR M-60 apparatus.

The roentgenograms were analytically indexed. The determination of the roentgenographic constants was made according to the DS lines corresponding to narrow angles of reflexion [9]. The exact determination of the parameters of the unit cell was made by extrapolating the parameters calculated by the method of Nelson and Riley [10, 11].

The determination of the activation energy of the final decomposition process was made by the method of Piloyan, devised for decomposition processes in which a gaseous phase arises [12]. Following this method, the relationship:

$$\ln m - 2 \ln T = A_0 - \frac{E}{RT} \tag{1}$$

is used, where m is the percentage weight loss of the sample, and T is the absolute temperature. The graphical representation of $\log m - 2 \log T$ as a function of $\frac{1}{T}$ must be a straight line whose slope yields the activation energy E.

The Piloyan relationship analogous to Eq. (1) and referring to DTA curves was not used, because the endothermal peak is overlapped by other heat effects.

Results

1. *Reactions of* $Sr(OH)_2 \cdot 8\,H_2O$ *on heating.* In the temperature range between 70 and 210° intense heat effects occur; for this reason the heat treatment of the octahydrate between 70 and 210° was carried out at a heating rate of 10°/min.

The loss of water of crystallization takes place within this temperature range, and is indicated by an endothermic peak on the DTA curve (Fig. 1a). This phenomenon is also indicated by corresponding inflections on the DTG and TG curves (Fig. 1a).

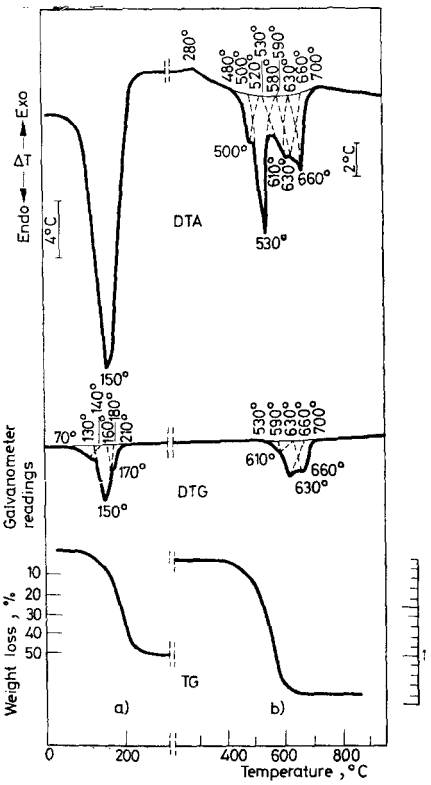

Fig. 1. TG, DTG and DTA curves of strontium hydroxide; a) $Sr(OH)_2 \cdot 8\,H_2O$ — heating rate 10°/min; sample weight = 0.632 g; b) $Sr(OH)_2$ — heating rate 5°/min; sample weight = 0.700 g

The analysis of the dehydration peaks on the three curves shows their complex form, revealing that this process takes place in several stages, characterized by different rates of water loss. These peaks were broken down into elementary processes, assuming that the DTG curve of each elementary process is symmetrical with respect to the ordinate of the maximum rate for each process. The following stages resulted:

The first dehydration process takes place between 70 and 140° with maximum rate at 110°. The water loss was calculated as follows: taking into account the symmetry of the process with respect to the ordinate of the maximum rate of water loss, the total loss is equal to twice the loss during the period of increasing

rate of the process (70–110°). A water loss of 13.4% resulted, corresponding to two moles of water of crystallization (theoretically 13.6%). The compound resulting from the reaction

$$Sr(OH)_2 \cdot 8\,H_2O \xrightarrow{-2\,H_2O} Sr(OH)_2 \cdot 6\,H_2O$$

appears to be $Sr(OH)_2 \cdot 6\,H_2O$ (Fig. 2).

The second dehydration step takes place in the range 130–180° with a maximum at 150°. The temperature range was established by extrapolating the DTG peak of this step to the points of intersection with the abscissa. The weight loss, calculated as in the first stage, is 34.2%, corresponding to 5 moles of water (theoretically 34%). The compound resulting after the second reaction:

$$Sr(OH)_2 \cdot 6\,H_2O \xrightarrow{-5\,H_2O} Sr(OH)_2 \cdot H_2O$$

is therefore the monohydrate.

The last dehydration stage occurs between 160 and 210° with a maximum rate at 170° corresponding to a water loss of 6.4% (one mole, theoretically 6.8%), in accordance with the reaction:

$$Sr(OH)_2 \cdot H_2O \xrightarrow{-H_2O} Sr(OH)_2$$

the result being amorphous strontium hydroxide.

At temperatures above 210°, reactions sometimes occur with reduced heat effects, and in this case the sensitivities of the DTG and DTA galvanometers were increased (Fig. 1b).

When amorphous strontium hydroxide is heated, it begins to crystallize at 280° in an exothermic reaction (Fig. 1b, DTA curve). An endothermic effect is produced at higher temperatures, with maximum at 500°, but without any weight loss. This can be attributed to a polymorphous transformation of $Sr(OH)_2$:

$$(\beta)Sr(OH)_2 \rightarrow (\alpha)Sr(OH)_2$$

The hydroxide melts at 530°, giving rise to an endothermic effect with no weight loss.

The decomposition of the anhydrous compound starts very slowly at 530°. This temperature can be determined from the inflection points of the DTG and TG curves (Fig. 1b). The reaction proceeds in several steps in the temperature range 530 to 700°, the residual compound being anhydrous strontium oxide.

The DTG curve of the final decomposition process provides two maxima, at 630° and 660°. The DTA curve also exhibits two maxima, at 610 and 660°.

The detailed study of these peaks shows that the first DTG peak at 630° has a flattened form below 630°, suggesting the overlapping of two decomposition steps with maxima at 600° and 640°.

On the other hand, the DTA curve shows a plateau at 640°, also suggesting the existence of two endothermal effects, with maxima at 640° and 660°.

All the above-mentioned facts indicate that the decomposition process takes place in three stages with maximum rates at 600°, 640° and 660°. The amounts of water lost in each stage were calculated, with the following results

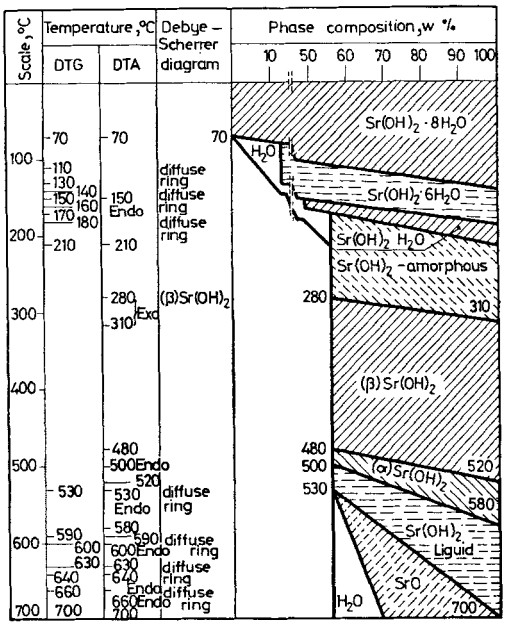

Fig. 2. Reaction of $Sr(OH)_2 \cdot 8\,H_2O$ to heat treatment.

The first stage occurs in the range 530 – 630° and corresponds to a water loss 3.5% (theoretically 3.7%), that is 0.25 H_2O:

$$4\,Sr(OH)_2 \xrightarrow{-H_2O} SrO + 3\,Sr(OH)_2$$

The second stage occurs within the range 590 – 660° with a maximum at 640°, and corresponds to a loss of 7% (theoretically 7.4%), that is 0.5 H_2O:

$$3\,Sr(OH)_2 \xrightarrow{-2\,H_2O} 2\,SrO + Sr(OH)_2$$

The third step takes place at temperatures between 630 and 700° with a water loss of 3.6% (theoretically 3.7%), which corresponds to 0.25 H_2O (Fig. 2):

$$Sr(OH)_2 \xrightarrow{-H_2O} SrO$$

This leads to the conclusion that the forces bonding the hydroxyl groups in the hydroxide are different. The activation energies of the three stages were calculated from the slopes of the straight lines with the use of Eq. (1) (Fig. 3). The

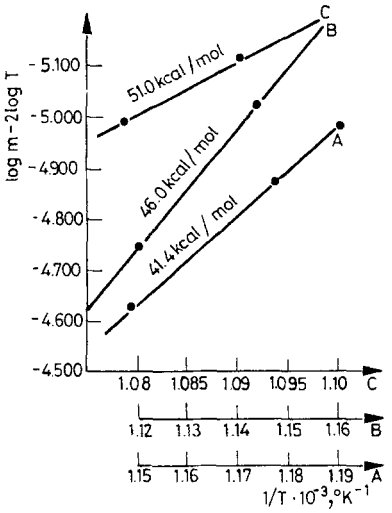

Fig. 3. Activation energy of the decomposition $Sr(OH)_2$

resulting E values were 41.4 – 51 kcal/mole, and there was little difference between the bond strengths (about 5 kcal/mole).

The strontium oxide resulting at 700° is amorphous, as shown in the DS diagram by the absence of interference lines. It does not crystallize below 1000°.

2. *Stabilities of compounds in the* $SrO-H_2O$ *system.* From the above-mentioned facts the following conclusions can be drawn as regards the stabilities of the compounds in the $SrO-H_2O$ system:

$Sr(OH)_2 \cdot 8\,H_2O$ is a crystalline compound stable up to 100°. On being maintained at 80° for 2 hours in a moist carbon dioxide-free atmosphere, the partially

Table 1

DS diagrams of $Sr(OH)_2 \cdot 8\,H_2O$ and (β) $Sr(OH)_2$

$Sr(OH)_2 \cdot 8\,H_2O$ Tetragonal system $a = 6.90$ Å $c = 5.20$ Å			(β) $Sr(OH)_2$ Tetragonal system $a = 4.10$ Å $c = 6.70$ Å		
I	*d*, Å	*hkl*	*I*	*d*, Å	*hkl*
vs	6.34	100	s	4.392	100
vs	4.290	101	ms	3.477	101
vs	3.551	200	s	2.840	110
w	3.186	111	s	2.480	102
vs	2.785	112	s	2.234	112
s	2.650	210			
s	2.547	002			

dehydrated octahydrate absorbed the lost amount of water stoichiometrically. The calculations made on the basis of the DS diagram confirm that it crystallizes in the tetragonal system with the unit cell constants $a = 6.90$ Å and $c = 5.20$ Å (Table 1).

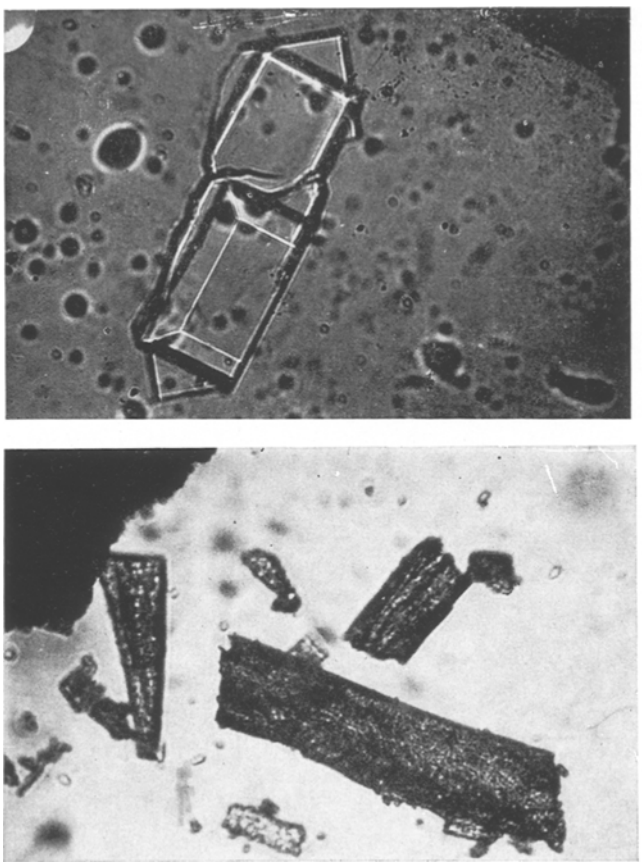

Fig. 4a. Micrograph of $Sr(OH)_2 \cdot 8\,H_2O$ (×480); b) Micrograph of $Sr(OH)_2$ (×480)

The micrograph in Fig. 4a shows the octahydrate crystallized from an aqueous suspension of strontium hydroxide.

$Sr(OH)_2 \cdot H_2O$ is a metastable compound between 160–210°. The monohydrate synthesized as shown on p. 466 could not be obtained in a crystalline form, nor could it be characterized roentgenographically; it was indicated only by its stoichiometric composition.

$Sr(OH)_2 \cdot 6\,H_2O$. The above-described thermal analysis reveals that the hexahydrate present at 130–180° (Fig. 1a, DTG curve) to a great extent overlaps

the temperature ranges in which the octahydrate and monohydrate exist. It therefore appears to be a labile compound, and has not been described earlier for this reason.

$Sr(OH)_2$. Anhydrous strontium hydroxide is stable in the range 210 – 540°. The product obtained by the procedure mentioned on p. 466 crystallizes at 280° to give the low-temperature form of (β)$Sr(OH)_2$. The micrograph in Fig. 4b shows this compound calcined at 400°. At 480° it may transform to a high-temperature form. It melts at 530°. $Sr(OH)_2$ crystallizes in the tetragonal system with the unit cell constants $a = 4.10$ Å and $c = 6.70$ Å (Table 1).

SrO. Anhydrous strontium oxide can be obtained in an amorphous form above 700° and even at 1000°.

Conclusions

1. Strontium hydroxide octahydrate dehydrates on heating, passing through the stages of hexahydrate and amorphous monohydrate.

2. $Sr(OH)_2$ exhibits two possible polymorphous forms; its decomposition, preceded by melting at 530°, takes place in three successive steps, characterized by activation energies of 41.4–51 kcal/mole.

3. Strontium oxide remains in an amorphous state even at 1000°.

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RÉSUMÉ — On a étudié le comportement thermique de l'hydroxyde de strontium octohydraté par analyse thermique, diffraction de rayons X et examen microscopique. Ce composé donne l'hexahydrate jusqu'à 210° puis le monohydrate. L'hydroxyde de strontium anhydre cristallise dans le système tétragonal et présente une transformation polymorphique à 480°. La déshydroxylation commence à 530° et s'effectue en 3 étapes. L'oxyde de strontium amorphe s'obtient à 700°.

ZUSAMMENFASSUNG — Das thermische Verhalten von Strontiumhydroxyd—Oktahydrat wurde röntgendiffraktometrisch, thermoanalytisch und durch optische Mikroskopie untersucht. Die Verbindung geht bis 210° in das Hexa- und daraufhin ins Monohydrat über. Die Anhydroverbindung kristallisiert tetragonal. Bei 480° erfolgt eine polymorphe Umwandlung. Über 530° verläuft eine Dehydroxylation in drei Stufen. Amorphes Strontiumoxyd wurde bei 700° erhalten.

Резюме — Изучено термическое поведение восьмиводной гидроокиси стронция методами термического анализа, рентгенодифракции и оптической микроскопии. Это соединение до 210° превращается в шестиводную гидроокись, а затем в моногидрат. Безводная гидроокись стронция кристаллизуется в тетрагональной системе и полиморфное превращение может происходить при 480°. Его дигидроксилирование начинается при 530° и проходит в три ступени. Аморфная окись стронция получается при 700°.