

The Transformation of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ into Lower Hydrates

BJØRN BERGTHORSSON

*Chemistry Department B, The Technical University of Denmark,
Building 301, DK-2800 Lyngby, Denmark*

In 1917 Richards and Yngve¹ reported that the temperature of transition for the system, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{sat. solution}$, could serve as a fixed point in thermometry ($61.341 \pm 0.001^\circ\text{C}$).

The following experiments show that a transformation of hexahydrate into dihydrate can be avoided if the hexahydrate crystals are grown at temperatures near by 61.3°C . If hexahydrate crystals were grown at 55°C , vapour pressure measurements showed that crystals originating only from one definite sample (four different samples were examined) gave dihydrate by heating. By growing the hexahydrate crystals at higher temperatures transformation into dihydrate could always be avoided irrespective of which of the four samples the hexahydrate crystals originated from. Vapour pressure measurements indicated that hexahydrate in this case transformed into monohydrate at approx. 71°C . Hexahydrate crystals, grown at 50°C or at lower temperatures, transformed always into dihydrate by heating.

In 1898 Richards² pointed out that the transition temperatures of salt hydrate systems could be used as fixed points in thermometry. His careful studies on $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are well known; the hydrate has since been used to standardize thermometers.

Richards and his collaborators often emphasized the importance of working with highly pure chemicals. They found³, *e.g.*, that 0.02 % NaCl in $\text{NaBr} \cdot 2\text{H}_2\text{O}$ gave a depression in the temperature of transition which was greater than the freezing point depression of a 0.02 % solution of NaCl in water. It is well known that van't Hoff accounted theoretically for the freezing point depression of solutions. Today it seems improbable that there exists a relation (generally valid for hydrate systems) between depressions of temperatures of transitions and quantities of impurities in solids. The increasing use of structural imperfections in explaining physical and chemical properties of solids indicates that detailed knowledge of structure is necessary to expound transformations.

Recently Jackson, Uhlmann and Hunt⁴ pointed out that the details of molecular configurations of interfaces are important, and that these details must be taken into account and treated properly in a valid theory of crystal

growth. This seems to be in agreement with the hastily growing use of details of structure in explaining properties of solids. The consequence of connecting structures of solids with molecular configurations of interfaces appears to be far reaching. A solid-liquid interface or a solid-vapour interface can be changed in different ways; in fact, it is often difficult to change experimental conditions and, at the same time, to avoid changing an interface. It may therefore be necessary to pay regard to the experimental conditions.

When the solubility of a solid in a liquid solution changes with temperature, the change may be expected to involve a change in the molecular configuration of the solid-liquid interface. Generally the influence of temperature on the solubility of hydrates in water is most pronounced for the highest hydrates. If, *e.g.*, the hexahydrate of strontium chloride is grown at 50° and at 60°C, the molecular configuration of the solid-liquid interfaces cannot be expected to be the same at both temperatures (see Table 1). We may expect

Table 1. The compositions of solutions saturated with respect to $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{SrCl}_2 \cdot x\text{H}_2\text{O}$ (the lowest hydrate).⁵ Values marked with* are own measurements.

<i>t</i> in °C	% SrCl_2 in saturated solution		
	Solid phase: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	Solid phase: $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$	Solid phase: $\text{SrCl}_2 \cdot x\text{H}_2\text{O}$
20.0	34.6		
30.0	36.9		
40.0	39.4	45.6*	
50.0	42.2		
55.0	43.9		
60.0	45.9		
61.3	46.5	46.5	
70.2	52.9*	47.3	52.9*
80		48.2	53.2*
90		49.5	
100		50.5	

to meet problems, when using hydrates to standardize thermometers, if connections exist between configurations of interfaces and defects of solids. This may be the reason for the fact that relatively few hydrates are in use today.

The following experiments indicate that a connection exists, at least in some cases, between the temperature at which a hydrate grows and the observed transformation phenomena.

EXPERIMENTAL DETAILS

Sample (I): $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, analyzed reagent (bought 1966) from J. T. Baker Chemical Co. U.S.A., Analysis: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ 100.4 %; insoluble matter 3×10^{-3} %; pH (of 5 % solution at 25°C) 6.6; SO_4^{2-} 5×10^{-4} %; Ba 5×10^{-4} %; Mg and alkalis (as sulphate) 5×10^{-2}

%; heavy metals (as Pb) 2×10^{-4} %; Fe 5×10^{-5} %. Sample (II): $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, for atomic absorption spectroscopy, from the British Drug Houses Ltd., England. Analysis: Ca 10^{-4} %; Cu 5×10^{-5} %; Fe 2×10^{-4} %; Pb 10^{-4} %; Mg 2×10^{-5} %; Zn 10^{-4} %; not less than 97 % $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. Sample (III): SrCl_2 , El-chemical (selectipur), from Merck, Germany. Analysis: Insoluble matter 5×10^{-3} %; Pb 2×10^{-4} %; Cu 2×10^{-4} %; Fe 5×10^{-4} %; Zn 2×10^{-4} %; Ca 10^{-2} %; Ba 2×10^{-4} %; PO_4^{3-} 2×10^{-4} %; N 10^{-3} %; not precipitated by $(\text{NH}_4)_2\text{CO}_3$ 0.3 %. Sample (IV): $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, analyzed reagent (bought 1968) from J. T. Baker Chemical Co. U.S.A. Analysis: The same as sample (I) except the following: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ 100.2 %; pH (of 5 % solution at 25°C) 5.3.

Table 2. Vapour pressures of saturated aqueous solutions of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{SrCl}_2 \cdot x\text{H}_2\text{O}$ (the lowest hydrate).

t in °C	p in mm Hg		
	Solid phase: $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ Found by others ^a	Solid phase: $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ Found by others ^a	Solid phase: $\text{SrCl}_2 \cdot x\text{H}_2\text{O}$
20.00	12.76		
25.00		13.06	
30.00	21.97	22.00	17.54
40.00	35.90	36.1	30.31
50.00	55.9	56.2	50.5
55.00	68.3	69.3	64.3
60.00	82.5	84.5	
61.32		86.3	
62.00	88.2		
65.00	97.3	102.0	103.0
66.00	99.9		87.3
69.00	107.7		
70.00	110.1	127.2	127.8
70.20			110.6
75.00			136.8
80.00		193.2	169.6

Vapour pressure measurements were used to identify a hydrate in a saturated solution. Once knowing the vapour pressures for the solutions saturated, respectively, with the three different hydrates (Table 2 and Fig. 2) it was possible to identify a hydrate in a saturated solution rapidly and easily. Whenever one pressure-temperature determination was insufficient in identifying a hydrate, *e.g.* in the neighbourhood of a temperature of transition, a pressure-temperature interval was determined.

The vapour pressures of the dihydrate system at temperatures below 61.3°C, the pressures of the hexahydrate system above 61.3°C and the pressures of the system with the lowest hydrate ($\text{SrCl}_2 \cdot x\text{H}_2\text{O}$ in Table 1 and Table 2; *cf.* "Results") at temperatures about 70°C have apparently not been measured before. The temperature of transition for the system, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot x\text{H}_2\text{O} + \text{sat. solution}$, was found to be $70.2 \pm 0.2^\circ\text{C}$ (Fig. 2). Sample (I) was used for these measurements.

With the aid of the Clausius-Clapeyron equation in the approximate form: $\Delta \ln p / \Delta(1/T) = -Q/R$ it can be shown that Q , for the system, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{sat. solution} + \text{water vapour}$, falls rapidly between 60° and 70°C. Q is equal to the negative value of the heat of formation of the quantity of solution containing one mole of solvent and $x/(1-x)$ mole of solute, in this case $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; the solvent from the gaseous, and the

solute from the solid form. Q may be written in the form: $Q=L-Sx/(1-x)$ where L is the heat of vaporization per mole of the pure solvent and S is the integral heat of solution per mole of solute to form a saturated solution. From the data in Table 1 it can be shown that $x/(1-x)$ rises rapidly as the temperature rises from 60° to 70°C giving a rapid fall in Q . At 25°C S is found to be 8670 cal per mole $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; this is nearly the same as the heat of fusion of 6 mol of ice (8618 cal).

The pyrex glass apparatus used in these experiments is illustrated in Fig. 1. The flask A (Vitreosil transparent quartz, Thermal Syndicate Ltd., England) contained 50–150 mg SrCl_2 , and variable quantities of water. The volume of A was approx. 6 cm³, and the inner diameter was about 1 cm. The flask D contained either $\text{NH}_4\text{HSO}_4 + \text{H}_2\text{O}$ (approx. 55 % NH_4HSO_4) or $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ (approx. 45 % H_2SO_4). The NH_4HSO_4 -solution was used for prolonged experiments, where repeated exhaustions for expulsion of foreign gases were necessary. The H_2SO_4 -solution was used for accurate vapour pressure, measurements.⁶ The volume of D was 100 cm³. The quantity of solution in D was approx. 70 ml.

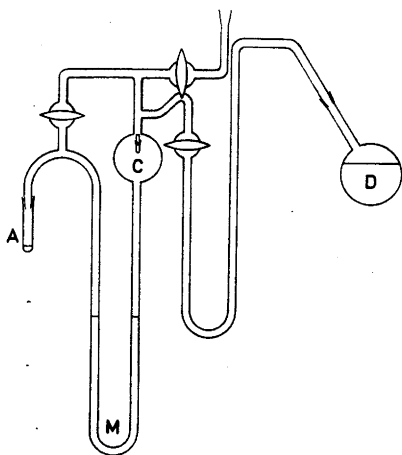


Fig. 1. Pyrex glass apparatus.

M is a manometer, containing silicone oil (Dow Corning 705, from Midland Silicones Ltd., England). The vapour pressures⁷ of the oil at the temperatures used are lower than 10^{-6} mm Hg. The specific gravity ρ at temperature $t^\circ\text{C}$ was found to be: $\rho = (1.1090 - 7.2 \times 10^{-4}t) \text{ g/cm}^3$. The inner diameter of the manometer tube was 0.8 cm. With the silicone oil in C (Fig. 1), the apparatus was evacuated, and the oil was heated to 100°C, before the flasks A and D were connected. The flasks were thoroughly cleansed before use. Vacuum grease (Apiezon H) was removed by means of chloroform. The flasks were thereafter filled with chromic acid cleaning solution, and left for one hour at 100°C. After washing with distilled water ($\kappa < 5 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$), the flasks were ready for use. Just before a SrCl_2 -solution was filtered through a glass filter (Scott and Gen; porosity G 5) into the flask A, the flask was washed four times with boiling distilled water, which was filtered through the glassfilter.

The solutions in A and D were cooled to 0°C before the first evacuation. Then they were gradually heated, and exhausted at intervals by means of a motordriven oil pump. If the solution in A and D were not cooled before evacuation, foreign gases in the apparatus caused bumping, which could result in washing off the vacuum grease from the joint into the solutions. It was absolutely necessary to prevent this. (If the flasks were first cleansed with a detergent and thereafter with chromic acid cleaning solution the tendency of bumping was much greater). A series of experiments was not started, until it was possible to exhaust the apparatus at 45°C without bumping.

By placing the flask D in one thermostat and the rest of the apparatus in another thermostat, it was possible to increase or decrease the concentration of a SrCl_2 -solution as desired. Concentrations were quickly and easily evaluated by measuring vapour pressures and temperatures. For accurate vapour pressure measurements the apparatus was placed in one thermostat.

The sulphuric acid solutions were analyzed for H_2SO_4 by titrating the acid. The analyzes checked within 0.07 of a percentage of composition, which gave an error of less than 0.2 %. The temperature was controlled within 0.02°C at the lowest temperatures (20°C) and within 0.15°C at the highest temperatures (80°C).

RESULTS

The experiments started three years ago with sample (I) (*cf.* Experimental Details). When hexahydrate crystals, originating from this sample, were heated in contact with a saturated solution, it was possible to avoid transforming hexahydrate into dihydrate, but only if the crystals were renewed at intervals in the following way: The heating started at 55°C with a quantity of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ which was suitably small (compared with the respective saturated solution) to be nearly all dissolved by 2 or 3° heating. Just before the crystals disappeared the heating was stopped and a new small quantity of crystals was grown, whereafter 2 or 3° heating could start again and so forth. Hexahydrate + saturated solution could be (stepwise) heated in this way up to approx. 71°C where a transformation into a lower hydrate occurred. Vapour pressure measurements indicated that this hydrate was a monohydrate.

This experience made probable that imperfections, which depended on growth conditions, could be made responsible for the transformation of hexahydrate into dihydrate. As it was desirable to find out whether foreign atoms had a part, three new samples ((II), (III) and (IV); *cf.* Experimental Details) were bought and examined. Sample (II) is the purest obtainable from The British Drughouses and sample (III) is the purest obtainable from Merck, Germany. Hexahydrate crystals, grown at 55°C or at higher temperatures and originating from these three new samples, did not give dihydrate by heating up to 68°C. Hexahydrate crystals, grown at 55°C and originating from (I), gave always dihydrate by heating up to 62–63°C. On the other hand hexahydrate crystals, grown at 50°C or at lower temperatures, gave always dihydrate before 68°C was reached irrespective of which sample the crystals originated from (*cf.* Table 3). These results strengthened the supposition that imperfections which depended on growth conditions (temperature) could be made responsible for the transformation into dihydrate. Now it appeared moreover probable that foreign atoms had a part in the phenomena observed when studying (I): It seemed probable that the before mentioned stepwise renewal of the hexahydrate crystals (from (I)) resulted in purer crystals that resembled the three other samples. The following experiments strengthened this supposition. Working with (I), all attempts at 69°, 68°, and 67°C to isolate the hexahydrate (by evaporating the liquid phase) resulted in generation of dihydrate. Although hexahydrate crystals (from (I)) in a saturated solution could be kept for at least two weeks at 68°C, it was not possible to dry the crystals even though the vapour pressure was only 0.4 mm Hg lower than the pressure of the saturated solution at the same temperature. This was easily

ascertained by measuring the equilibrium pressure. On the other hand it was possible to dry hexahydrate crystals from (III) at 66°C at a vapour pressure 1 mm Hg lower than the pressure of the saturated solution. These experiments seemed to indicate also that chemical impurities in sample (I) (concentrated by evaporation) could be made responsible for the transformation of hexahydrate into dihydrate.

It may be expected to be difficult to determine the part of foreign atoms at low impurity concentrations because of interactions between imperfections in a crystal; however, chemical impurities may have a dominating role at higher concentrations. Phenomena connected with (I) could be explained in this way, *i.e.*, that the presence of chemical impurities was necessary for generation of dihydrate, if hexahydrate crystals were grown at 55°C or at higher temperatures (*cf.* Table 3).

Table 3. Results of heating hexahydrate crystals grown at different temperatures.

Temperature (°C) at which SrCl ₂ ·6H ₂ O-crystals were grown	Phenomena observed when SrCl ₂ ·6H ₂ O-crystals from the four different samples were heated			
	I	II	III without and with impurities.	IV
≤ 50	Dihydrate created below 63°C.	Dihydrate created below 66°C.	Dihydrate created below 68°C.	Dihydrate created below 66°C.
55	Dihydrate created below 63°C.	No dihydrate generated below 68°C.		
> 55	Stepwise renewal of crystals prevented generation of dihydrate	No dihydrate generated below 68°C.		
> 55	Stepwise renewal of crystals gave in all four cases a hydrate with less than 2H ₂ O at approx. 71°C ((III) without impurities; (III) with impurities were not heated above 68°C).			

Therefore, experiments were now made, the purpose being to find out which chemical impurities contributed to the transformation of hexahydrate into dihydrate. Foreign substances were added to (III) trying to imitate phenomena connected with (I). Sample (III) was chosen because hexahydrate

crystals from (III), grown at 50°C , transformed into dihydrate at the highest temperature (*cf.* Table 3). The experiments (with and without added chemical impurities) were performed as follows: Hexahydrate crystals, generated in a supersaturated solution at 0°C , were nearly quantitatively dissolved at temperatures between 58 and 61°C . The small crystals were then grown by cooling $2-3^\circ$, and then again nearly all was dissolved by heating (to remove crystals grown at 0°C). The system was now cooled to 55°C . At this temperature the water was evaporated for 5 h giving approx. 100 mg $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ -crystals. The vapour pressure at which the crystals were grown was 0.6 mm Hg below the pressure of the saturated solution. Before the crystals were heated, the vapour pressure was raised 0.3 mm Hg above the pressure of the saturated solution for 5 min. This was to assure that the pressure during heating would be the same as that of the saturated solution (Fig. 2, curve 1).

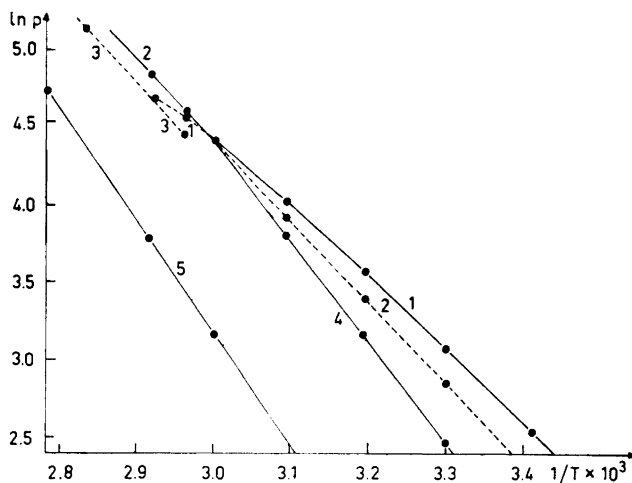


Fig. 2. 1, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ —sat. solution. 2, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ —sat. solution. 3, The lowest hydrate—sat. solution. 4, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ — $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. 5, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ — $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$. The curves 1 and 2 intersect at 61.3°C ; the curves 1 and 3 intersect at 70.2°C . (— — —) new data, (—) found by Collins *et al.*⁸.

Calcium and barium are the two impurities, which are the most difficult to eliminate from salts of strontium. Therefore experiments were performed where different quantities of the chlorides of Ca or Ba were added to (III), but it did not result in giving dihydrate by heating up to 68°C . Then it was examined if SrSO_4 could be made responsible for giving dihydrate, but $10^{-3}\%$ Na_2SO_4 did not result in dihydrate either. Traces of lead, zink, and magnesium were found spectroscopically in sample (I). The chlorides of these metals were added to (III) and examined one by one, but no dihydrate was generated. Variable quantities of HCl and NaOH were added, but always without generation of dihydrate. An addition of 0.5 % FeCl_2 , 0.5 % FeCl_3 , and 0.1 % NaCl, NaBr,

LiCl or of Na_2CO_3 to (III) did not contribute to generation of dihydrate either (cf. Table 3).

It proved to be difficult to isolate the lowest hydrate from a saturated solution originating from (I). If, *e.g.*, the crystals of the lowest hydrate were dried by evaporating the saturated solution at 70°C , dihydrate was generated; at 80°C dihydrate crystals were also generated, when the crystals of the lowest hydrate were dried at vapour pressure 4 mm Hg below the pressure of the saturated solution. However, if the hydrate was dried at a pressure 1 mm Hg below the pressure of the saturated solution (at 80°C), dihydrate was not generated. In this way crystals were dried for 72 h whereafter the Cl^- content was determined by means of Volhards method; it was found to be 38.7 % corresponding to the composition $\text{SrCl}_2 \cdot 1.37\text{H}_2\text{O}$. This high water content, compared with $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, is possibly due to insufficient drying. However, it is noteworthy that the vapour pressure was 168.6 mm Hg at 80°C . The equilibrium pressure of the hydrate pair monohydrate-dihydrate at 80°C is 80.0 mm Hg;⁸ this is less than half of the pressure at which the hydrate was dried (Table 2 and Fig. 2). It is possible that the crystals contain more than one mole of water at this high vapour pressure.

Dihydrate crystals (originating from I), which were dried for four days at 45°C (16°C below the temperature of transition) by bringing the pressure 3 mm Hg below the pressure of the saturated solution (Table 2 and Fig. 2), gave also a high water content. Two determinations gave 2.09 and 2.14 mol H_2O per mol hydrate, respectively. These results give a hint of a need for experiments with the object of finding out whether the hydrates are nonstoichiometric compounds.

DISCUSSION

Although it has not yet been possible to find foreign substances which can be made responsible for the transformation of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ crystals (grown at 55°C or at higher temperatures and then heated as described in Results) into $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, it appears probable that foreign substances can be made responsible for the transformation of hexahydrate from (I) into dihydrate (cf. Table 3). It seems possible that the presence of chemical impurities is necessary for generation of dihydrate, if the hexahydrate crystals are grown at 55°C or at higher temperatures and then heated as described. If, on the other hand, highly pure hexahydrate crystals are grown at 50°C or at lower temperatures, the role of chemical impurities is not so clear; other types of imperfections, which depend on temperature, may have a part. It will probably be necessary to pay regard to interactions between imperfections in highly pure hexahydrate crystals, and to pay regard to non-equilibrium conditions, when crystals, which have been grown at definite temperature, are heated.

Diffusion rates for atomic imperfections in solids are often very low. If a crystal at equilibrium (imperfection equilibrium) is heated or cooled, the result may therefore be a long lasting non-equilibrium condition. Measurements of equilibrium pressures of hydrate pairs, which are to be found in the literature, indicate that non-equilibrium conditions sometimes prevail. Collins and Menzies⁸ found, *e.g.* that difficulties, encountered in measurements, became

less apparent the higher the temperature. They found that material, which had for purposes of measurement previously been in contact with a higher pressure of water vapour at a higher temperature, was prone to yield too high pressure values at subsequent lower temperature measurements. Nitta and Seki⁹ found a difference in the dissociation pressure of strontium formate dihydrate when measured with ascending and descending temperatures.

Further experiments may therefore show that the heating of the hexahydrate crystals brings about non-equilibrium conditions, which involve a generation of dihydrate; the described renewal of crystals at proper temperature intervals is possibly one of the easiest methods used in avoiding such non-equilibrium conditions.

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