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The Phase Diagram of Sodium Chloride and Steam Above the Critical Point

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It is well known that high pressure steam dissolves several solids, such as sodium chloride, silica, *etc.* This has caused great trouble in power plants operating with higher steam pressure than 75 kg/cm^2, as the dissolved substances will deposit on the turbine blades, heavily impairing their efficiency. Our original purpose was to ascertain the solubility of sodium chloride in steam at higher temperatures and pressures than were previously measured, but we have also studied the displacement of the critical phenomena, when salt is added to the water.

An extensive review of the work hitherto carried out in this field has recently been published by Booth and Bidwell [1], so it will be sufficient for us to direct the attention of the reader to the work of Spillner [2] and of Straub [3], both of whom investigated the salt contents of the steam phase by its electrical conductivity after cooling. Spillner also measured the dielectric constant of steam. He found that the conductivity of the solution of salt in steam was very small, so the electrolytic dissociation must be negligible, as could be expected from the low dielectric constant, the latter being only about 2.9 at the critical point. Schröer [4] measured the raising of the critical temperature when various halides were added to the water.

EXPERIMENTAL

Our measurements were carried out in a steel bomb, Fig. 1, which was lined with copper, about 5 mm thick. The steel was delivered by Wikmanshyttan. The quality used, VH 312, should, according to Swedish standards, contain 0.23—0.28 % C, 0.15—0.35 % Si, 0.50—0.80 % Mn, 0.9—1.2 % Cr

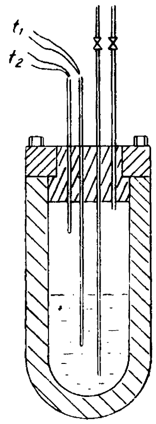

Fig. 1. High pressure vessel.

and 0.15—0.25 % Mo. Its tensile strength was ca. 72 kg/mm^2 at 500° C (communication from the steel work). The volume of the bomb was a little more than 5 litres. The bomb was heated by an electrical winding and was insulated with kieselguhr. The temperature was measured to 1° C with chromel-alumel-thermocouples, calibrated at the melting points of Sn, Pb and Zn. Two couples were situated in borings in the upper and lower part of the bomb and two were inside tubes running through the cover of the bomb and ending at different heights inside it. Usually the four thermocouples differed by only 1° C or less. The pressure was read to 1 kg/cm^2 on a Bourdon manometer calibrated by The Government Testing Institute, Stockholm, twice during the course of the investigation.

Samples were let out from the bomb through copper capillaries with 1 mm inner diameter, one ending near the top, the other near the bottom of the bomb. The capillaries passed through cooling mantles before the liquid was discharged through steel valves. Before a sample was taken for analysis an adequate quantity was let out through the capillary and discarded, in order to ensure that the sample gave the true composition of the phase in which the capillary ended. The chloride ion was titrated with silver nitrate using chromate as an indicator. The concentrations are given in weight per cent. The density of the high temperature phases was not measured, so the concentration in them cannot be given.

The bomb was filled through a steel pump. Both this and the steel valves rusted of course, but the iron hydroxide formed does not affect the measurements. The copper lining was also somewhat attacked, and especially the samples from the bottom of the bomb were usually more or less turbid from some cuprous chloride and oxide. Presumably these compounds precipitated during the cooling of the sample and were kept in solution as complex compounds in the hot interior of the bomb. Their amount was so small that they cannot possible have interfered with the measurements. Of course there are much better materials than copper, but the vessel was available from an earlier investigation of technical nature concerning the possibility of making potable water from sea water by distillation at high pressure [5].

After the bomb was filled with a solution, it was heated, during which procedure liquid had to be let out. When the required temperature was reached and equilibrium established, samples were let out through the two capillaries, ending in the upper and lower part of the vessel. At the beginning these had the same composition, but below a certain pressure the contents parted into two phases, one at the bottom, being richer in salt, and another at the top with less salt. Near this critical pressure samples were taken at every kg/cm^2. Between the taking of every pair of samples at least 30 minutes were allowed to pass, often much more, in order to re-establish temperature equilibrium and allow the two phases to separate completely. With sinking pressure the lower phase became richer in salt, but the sampling had to be interrupted when its salt content exceeded 26 %, which is the solubility at room temperature, to avoid the capillary being obstructed by precipitated salt. The upper phase was sampled down to pressures about 150 kg/cm^2, where its salt content was of the order of magnitude 0.005 %.

MEASUREMENTS

Runs were made at intervals of about 10° from 353° C to 475° C. At temperatures higher than 445°, however, samples were taken only from the upper phase. In most cases two or three runs were carried out at every temperature. Samples were taken at every kg/cm^2 near the pressure at which the separation into two phases occurred, then at every 5 kg/cm^2, but at those pressures where only the upper phase was investigated at every 10 kg/cm^2. For every temperature the salt contents were plotted against the pressure and a smoothed curve drawn. Some of these are given in Fig. 2. At temperatures higher than 374° C, the critical temperature of pure water, the curves for the two phases will meet at a critical point, which corresponds to the highest pressure under which two phases can exist at that temperature.

In order to obtain this critical turning-point to the right of each curve one has to choose a definite critical composition of the solution, which is richer in salt the higher the temperature is. If a different composition is used, the formation of two phases will occur at a lower pressure and the middle part

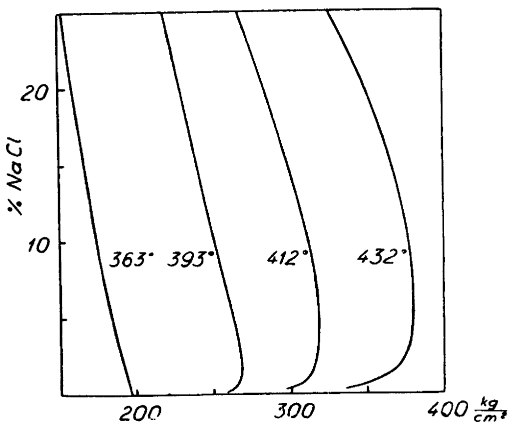

Fig. 2. Salt content of liquid, p—c-diagram.

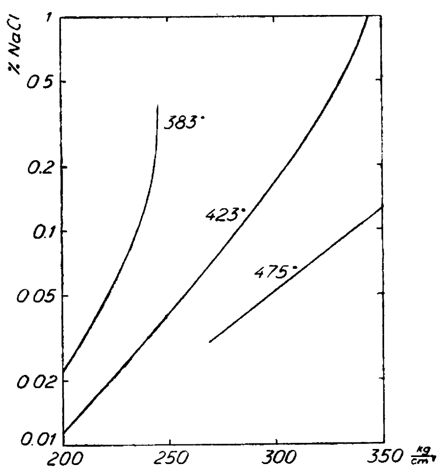

Fig. 3. Salt content of steam, p—log c-diagram.

of the curve is lost. The critical composition is obtained if the mean value of the compositions of the two phases is also plotted in the diagram. This gives a slightly bent curve which is extended to the critical pressure at that temperature. This pressure could be ascertained to within $\pm$ 1 kg/cm², as the pressure of separation was changed only a little if the original composition was not too far from the critical one. After a few preliminary experiments it was then possible to chose the correct solution for each temperature.

The logarithms of the salt contents of the upper phase, mostly less than 1 %, were also plotted against the pressure, whereby rather straight lines were obtained, Fig. 3. When all the results were plotted it was seen that the mean deviation of the measured points from the mean curves was about $\pm$ 2 kg/cm². Our measurements agree well with Spillner's few measurements at 407° C [2].

If the compositions of the phases are plotted against the temperature, we get, for each constant pressure, a curve showing the temperature *above* which two phases will occur.

At temperatures lower than 374° C the curves in Fig. 2 will start at zero salt concentration and the vapour pressure of pure water, as is shown for 363° C. This curve gives the vapour pressure of solutions up to 25 % NaCl. The steam above these solutions also contains some sodium chloride, but the amount is so small that it cannot be shown in the same figure. Fig. 4 gives the salt concentrations at two temperatures. These results are much less accurate than the other measurements. Sometimes greater concentrations were found

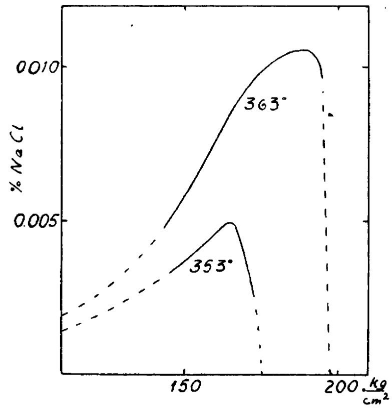

Fig. 4. Salt content of steam, p—c-diagram.

which is believed to be due to drops of the liquid solution being dragged along with the steam. The dashed parts of the curves are extrapolated.

Spillner [2] found that the steam containing salt had no electrical conductivity so there are no ions in it, but NaCl-molecules. He also measured the dielectric constant at the critical point to be 2.9, so that this water should be regarded as a "non-aqueous solvent".

RESULTS

From the smoothed curves obtained by plotting the concentration against pressure the critical compositions were found as mentioned above and these values plotted against temperature and pressure. A smoothed curve was drawn again, from which the plotted points only deviated by 0.1 %. The smoothed values are:

Table 1. Critical curve for NaCl-solutions.

% NaCl	0	0.2	0.5	1.0	1.5	2.0	3	4	5	6	7
$t°$ C	374	379.5	383.5	388.5	394	399	408.5	416.5	424	431	437.5
p kg/cm²	224	239	248	259	271	283	309	332	354	376	397

If the values of the last two lines are plotted in a p-t-diagram a curve is obtained which forms a continuation of the vapour pressure curve of pure water, the uppermost curves in Figs. 5 and 6.

In this p-t-diagram were also plotted the smoothed pressure values corresponding to different concentrations, for all temperatures investigated. The resulting curves for the lower, concentrated phase are given in Fig. 5,

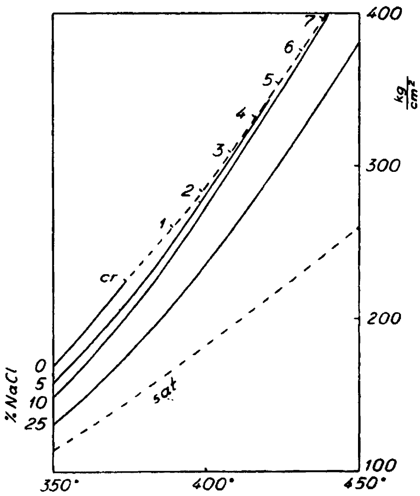

Fig. 5. Salt content of liquid, t—p-diagram.

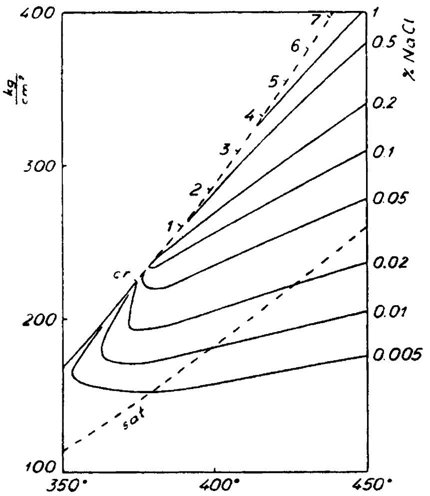

Fig. 6. Salt content of steam, t—p-diagram.

and for the upper steam phase in Fig. 6. The values, once more smoothed, are contained in Table 2. The broken line crossing the table indicates the place of the critical states, the pressures of which are given in the second line. The numbers above the broken line refer to steam hotter than 374° C, those below it to the phase at the bottom of the vessel.

In one experiment steam was let out from the vessel until the solution was saturated. This was indicated by the fact that, after letting out more steam, and raising the temperature to its original value before the letting out, the former pressure was restored. It was also found that the capillary outlet from the bottom was choked by salt, so it was difficult to pump more solution into the vessel. The pressures of the saturated solutions are given in the last line of Table 2 and the corresponding curve drawn in Figs. 5 and 6.

In the experiments in which the pressure became less than that of the saturated solution, the lower phase could not more be liquid, but was solid sodium chloride. Regarded as a phase diagram, Figs. 5 and 6 show three areas: at the left top a one-phase area, in the middle an area of two phases, liquid and steam, and at the right bottom the area of solid salt and superheated steam.

Table 3 gives approximate values of the salt contents of steam at three temperatures below the critical point of pure water in *parts per million*. Table 4 gives in *per cent* the salt contents of the solutions in equilibrium with the

Table 2. Pressure at which a phase exists containing the amount of salt shown in the first column.

t =	350	360	370	380	390	400	410	420	430	440	450	460	475° C
Crit. Pr.				240	262	286	313	343	373	405	436		
0 %	169	191	215										
0.005 %				149	154	159	163	166	169	171			
0.01				172	178	184	190	194	198	202	205	208	
0.02				193	199	206	213	220	226	231	236	241	
0.03				206	211	218	227	234	241	248	254	259	267
0.05				220	226	234	243	252	261	269	277	285	296
0.1				234	242	253	264	275	286	297	308	318	334
0.2				240	254	268	233	297	311	325	338	352	372
0.5	167	189	213	240	260	280	301	321	341	361	379	396	
1.0	166	187	211	236	262	284	309	333	358	382			
2.0	163	184	208	234	262	286	313	340	368	396			
5.0	157	178	201	226	254	283	313	343	373	403			
10	148	169	192	216	244	284	305	338	371	405			
15	140	161	184	208	233	261	291	324	369	395			
20	133	154	176	199	222	248	277	309	341	376			
25	127	147	168	189	211	235	260	289	321	256			
sat.	113	127	141	155	169	183	198	213	227	243	258	273	297

Table 3. Approximate salt content of steam below the critical point of pure water (in parts per million)

p kg/cm^2	353°	363°	372°
140	30		
150	37		
160	46	77	
165	50		
170	35	93	105
175	0		
180		101	140
190		106	180
195		90	
198		0	
200			200
205			260
210			100
211			88
220			0

Table 4. Salt content of solutions in equilibrium with the steams recorded in Table 3 (in per cent)

353°	363°	372° C
21.8		
13.5	26	
7.0	18.8	
4.3	15.4	
1.9	12.3	27
0	9.2	24
	7.0	20.7
	2.9	14.3
	1.0	11.4
	0	9.7
		8.5
		5.9
		3.4
		3.0
		0

steams in Table 3 at the same temperatures and pressures. If the compositions of the two co-existing phases at some temperature above 374° are wanted, they can easily be obtained if the composition-pressure curve for that temperature is drawn, when they are found as the two values of the curve for a given pressure.

These results give an answer to the problem as to whether it is possible to free the steam from a boiler from the salt it has dissolved which is of interest in steam engineering (cf. the introduction). Spillner and others [2] are of the opinion that it is not possible to wash out the salt with feed water, but Straub [3] succeeded in purifying the steam to a high degree by running the steam through a small fractionating column with four bubble cap plates, and even with a column with only one single plate. If a phase diagram (*c*—*t*-diagram) is constructed from the measurements in this investigation, it will be seen, that the steam with salt (*cf.* Tables 3 and 4, *e. g.* at 170 kg/cm²) will be in equilibrium with a water very much more rich in salt. Our results thus support Straub's, and it should be possible to wash the steam free from salt in a scrubber, provided the pressure is lower than 224 kg/cm², the critical pressure for pure water.

The results show that a salt solution at 300 kg/cm² and 475° C yields a steam with a little more than 0.05 % NaCl and a liquid which is almost saturated at room temperature. The advantage of this distillation procedure according to an invention by Baltzar von Platen is that the thermal efficiency is much better at this pressure and temperature than at atmospheric pressure. [5] Mr von Platen considers that water with 0.05 % NaCl, obtained from sea water, could be used for drinking and irrigation in places where potable water is scarce. A further purification by means of ion exchanger would be rather cheap. Such water could be immediately used as boiler water as the solubility of calcium and magnesium ions in the steam is very small. We have distilled sea water from Skagerrak at the west coast of Sweden with a chlorosity [6] of 14.72 g Cl^-/lit. at 300 kg/cm² and 450° C. The distillate contained 0.62 g/lit. Cl^-, $2.9 \cdot 10^{-4}$ mol/lit. $Ca^{2+} + Mg^{2+}$ (mean values from two experiments) and no sulphate ion detectable with barium salt.

SUMMARY

The phase diagram of the system sodium chloride — water — steam has been investigated in the region 353°—475° C and 150—400 kg/cm². Values are given for the vapour pressures of solutions and the solubilities of sodium chloride in steam.

A new method of making potable water from sea water is mentioned.

The apparatus was attended by Mr Fritz Wallin and Mr Gustav Eriksson. The analyses were carried out by Mr Ane Swärdh. During the last part of the investigation Baron Casper Wrede, Mr Hans Dinger and Mr Erik Lundblad also took part in the work.

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