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THE SYSTEM H_2O–NaCl AT ELEVATED TEMPERATURES AND PRESSURES*

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ABSTRACT. The system H_2O–NaCl has been studied to pressures of 1240 bars and through the temperature interval 250°-700°C. We have determined the temperature and pressure of the gas-solid-liquid boundary curve. The solubility of solid NaCl in steam up to saturation pressures has been measured. The composition of coexisting gases and liquids at pressures above the melting pressure and below the critical pressure has been determined for isotherms ranging from 350°-700°C. The critical composition and pressure for various isotherms have been determined. The NaCl concentration of saline hot springs is not inconsistent with the postulate that the sodium chloride was transported from the magmatic hearth in gaseous H_2O.

INTRODUCTION

Our interest in the system H_2O–NaCl stems from a variety of considerations. Some proposals are current for the production of power by detonating a fission or fusion device in an underground salt bed or salt dome. The energy released will melt a quantity of NaCl. High pressure water, admitted to this body of molten salt will be converted to steam. A knowledge of temperatures, pressures, and compositions of coexisting liquids and vapors is needed to evaluate such a system. Various methods of sea water demineralization have been proposed that involve evaporations at high temperatures and high pressures. Values for equilibrium concentration of salt in vapor are thus needed.

The system H_2O–NaCl is of fundamental physiochemical interest. It has long been known that systems of two components fall into two contrasting classes. One class of systems shows a continuous three-phase surface and a continuous critical curve that extends from the critical temperature and pressure of one of the components to that of the other component. The second class of systems shows a discontinuous three-phase region and a discontinuous critical curve ending in two critical end points. Prior to this work, no inorganic system of either of these two classes has been studied through the critical region. The system H_2O–NaCl illustrates the case of the continuous critical curve, and the system H_2O–SiO_2 (Kennedy, Wasserburg, Heard and Newton, in press), which has just been completed, illustrates the case of the discontinuous critical surface and discontinuous critical curve ending in two critical end points, with two three-phase regions.

Certain features of the system H_2O–NaCl are directly applicable to the problem of the origin of hot spring and geyser waters. This will be discussed in a later section of this paper.

PREVIOUS WORK

Keevil (1942) has shown that the binary system H_2O–NaCl belongs to the class of systems in which a continuous three-phase surface extends from the pure H_2O end of the system to the pure NaCl end. Thus the saturation curve for the aqueous sodium chloride solution is continuous up to the melting point

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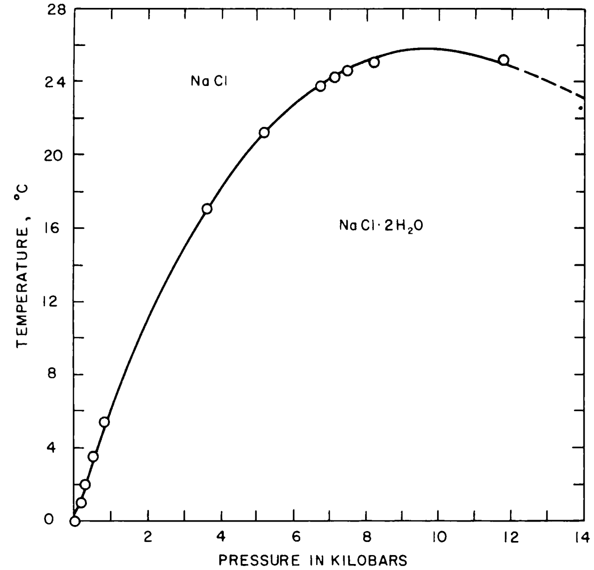

Fig. 1. The influence of pressure on the incongruent melting of $NaCl \cdot 2H_2O$. Data of Adams and Gibson (1930). The two points where the line for 25°C crosses the curve correspond to the pressures between which the dihydrate is the stable phase (see fig. 2) at 25°C.

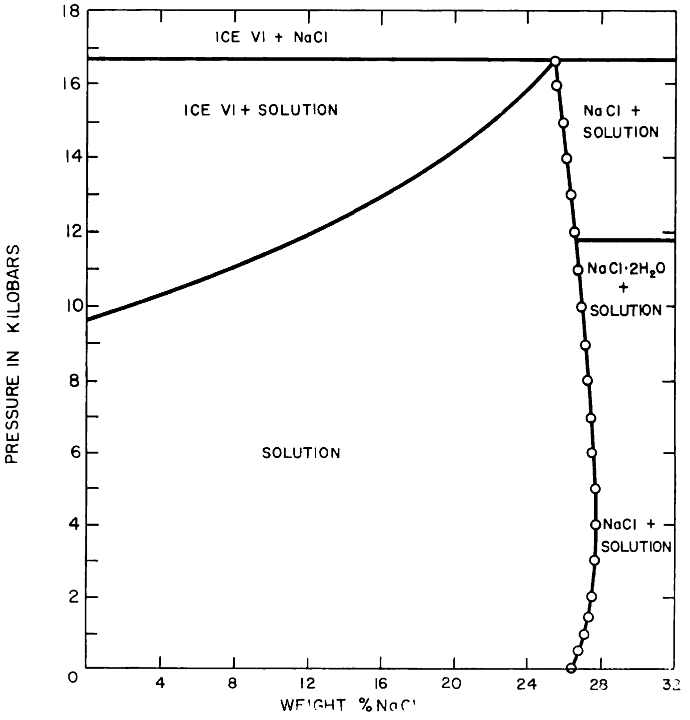

Fig. 2. Equilibrium diagram for the system $NaCl–H_2O$ under pressure at 25°C; after Adams.

of the salt. The critical curve is at higher pressures than the saturation curve. Critical phenomena are shown only by unsaturated solutions.

Adams and Gibson (1930) have shown that the eutectic in the system H_2O–NaCl is at –21.1°C. The solid phases present are ice plus the hydrate $NaCl \cdot 2H_2O$. Liquid in equilibrium with the two solid phases at the eutectic point contains 23.3 wt percent sodium chloride. The cryohydrate melts incongruently at 0.1°C to crystalline NaCl, and a liquid containing 26.3 wt percent sodium chloride.

Adams and Gibson (1930) have determined the incongruent melting of $NaCl \cdot 2H_2O$ up to 12,000 bars. Their data are plotted in figure 1. The results of Adams and Gibson on the system $NaCl \cdot 2H_2O$ are most surprising and, as far as we know, unique among hydrates. We know of no other case where the value of $\Delta s/\Delta v$ for a hydrate changes from sharply positive to negative over a narrow pressure interval, as indicated in this figure.

Adams (1931) has also determined the equilibrium diagram for the system H_2O–NaCl at 25°C up to 16,000 bars. These results are shown in figure 2.

The generalized phase diagram for a binary system, A–B over a wide range in temperatures and pressures of the type water-sodium chloride, has been discussed by Morey (1957). Figure 3 is a projection of the three-dimensional model showing pressure-temperature-composition. The curve L_A + A shows the change in melting point of solid A with pressure. G + L_A shows the vapor pressure of pure A ending at the critical point of A, namely A_C. These two curves intersect at the triple point of A, namely A_t. The curve G +

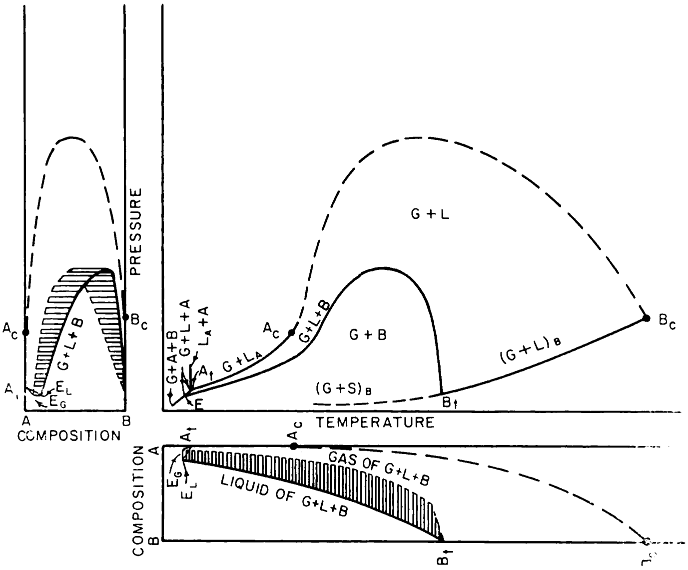

Fig. 3. Projections of a solid pressure-temperature-composition model for a binary system A–B, where no compounds are formed; there is no liquid immiscibility and the solubility curve does not intersect the critical curve.

L + A also radiates from the triple point to the eutectic at E. G + A + B extends from the eutectic E to lower temperatures and pressures. The curve G + L + B also extends from the eutectic. This curve rises to a maximum and then falls to the triple point of B at B_t. The curve G + L + B shows the vapor pressure of saturated solutions in the composition A-B at different temperatures. The vapor pressure curves of solid B and liquid B also extend from the eutectic B_t. These are the binary curves $(G + S)_B$ and $(G + L)_B$. These two curves show the vapor pressure curve for solid B and the vapor pressure curve for liquid B. The curve $(G + L)_B$ ends at the critical point of B, B_C. The curve A_CB_C, which extends from the critical points of the pure components, A and B, shows the distribution of critical points of various compositions in the system A–B.

The eutectic E appears as two points in the T-x and P-x projections. These two points show the coexisting compositions of the gas and liquid phases at the eutectic. Curves A_tE_G and A_tE_L show the compositions of gases and liquids that coexist with solid A down to the eutectic. The curves E_GB_t and E_LB_t show compositions of gases and liquids coexisting with B from the eutectic to the triple point of B at B_t.

The regions G + B and G + L show the stable fields of gas + liquid and gas + solid. In the system H_2O–NaCl, the solid phase is crystalline sodium chloride. The gas is steam with dissolved sodium chloride, and in the G + L region the liquid phase is an unsaturated solution of sodium chloride in water. The G + L region is bounded by the critical curve.

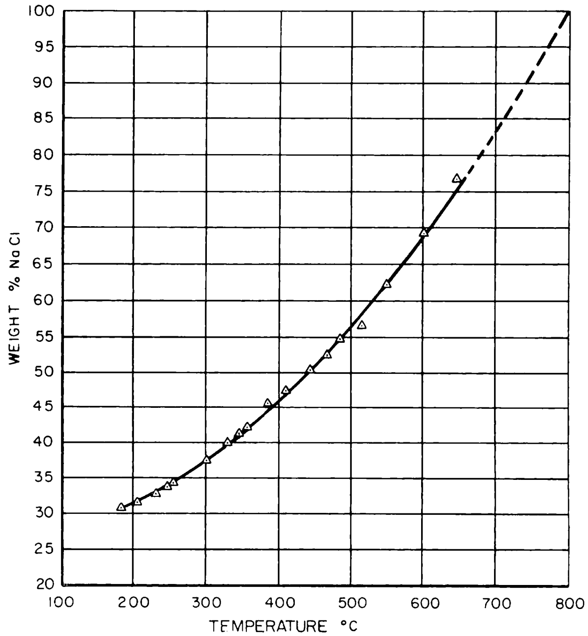

Fig. 4. Composition of the liquid phase of saturated aqueous sodium chloride solutions. Data from Keevil.

Only a limited portion of the system H_2O–NaCl above room temperatures has been studied prior to this work. Keevil (1942) has determined the three-phase vapor pressure and the composition of the liquid phase of saturated aqueous solutions of sodium chloride in the temperature range 180°-650°C. We have not redetermined the composition of saturated aqueous solutions of sodium chloride over this temperature interval and have relied on Keevil's data. Keevil's data on the composition of the saturated liquid NaCl solutions

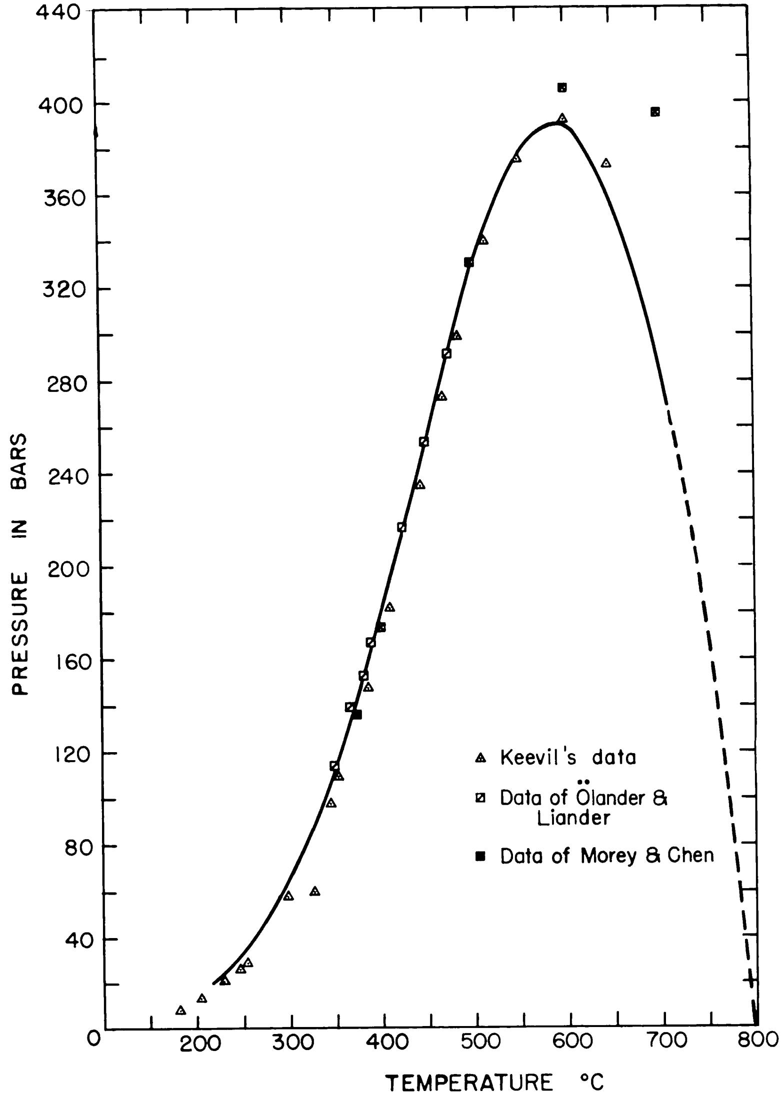

Fig. 5. Three-phase vapor pressures in system H_2O–NaCl showing our curve and results of Keevil, Olander and Liander, and Morey and Chen.

are shown in figure 4. Keevil's determinations, those by Ölander and Liander (1950), and determinations by Morey and Chen (1956) are shown in figure 5. The solid line in figure 5 represents our current determinations of the best value of vapor pressure. Our determinations, made on both a rising and a falling temperature cycle, are shown in figure 6.

Ölander and Liander (1950) also studied phase equilibrium relations of sodium chloride solutions above the critical point of water. They determined the critical end points for isotherms ranging from 380°-440°C, and they studied compositions of gases in equilibrium with solid NaCl between 350°

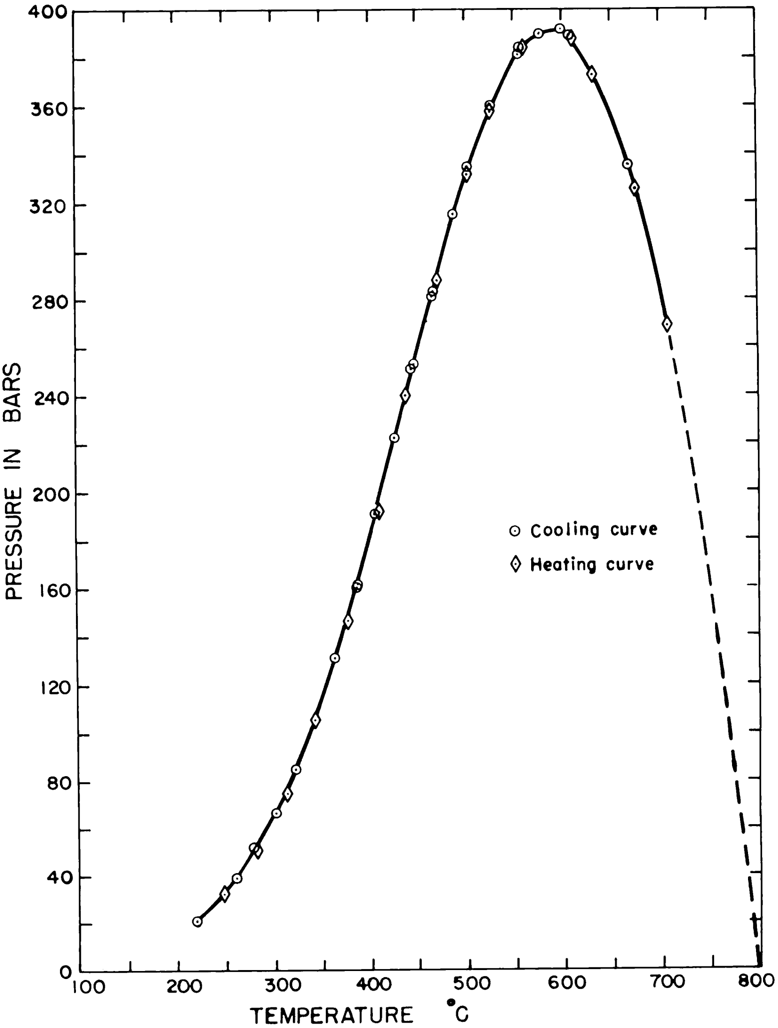

Fig. 6. Determinations of three-phase vapor pressures in system H_2O–NaCl made on rising and falling temperatures.

and 380°C. Our results are in only fair agreement with the results of Ölander and Liander; however, there is no systematic deviation between our data and theirs. Styrikovich, Khaibullin, and Zkhvirashvily (1955) have determined the solubility of sodium chloride in superheated steam in the temperature interval 400°-550°C and through the pressure interval 30-180 bars. Their method was a dynamic and not a static method, and results of their investigations are not directly comparable to ours. Other papers have appeared by Styrikovich (1957) and Styrikovich and Khaibullin (1956). Copeland, Silverman, and Benson (1953) have measured the densities of gases and liquids in the system H_2O–NaCl over the temperature interval 385°-396°C. Benson, Copeland, and Pearson (1953) also calculated apparent molal volumes, partial molal volumes, and compressibilities of the H_2O–NaCl system over the same temperature region, 385°-396°C. Data on phase relations over essentially the

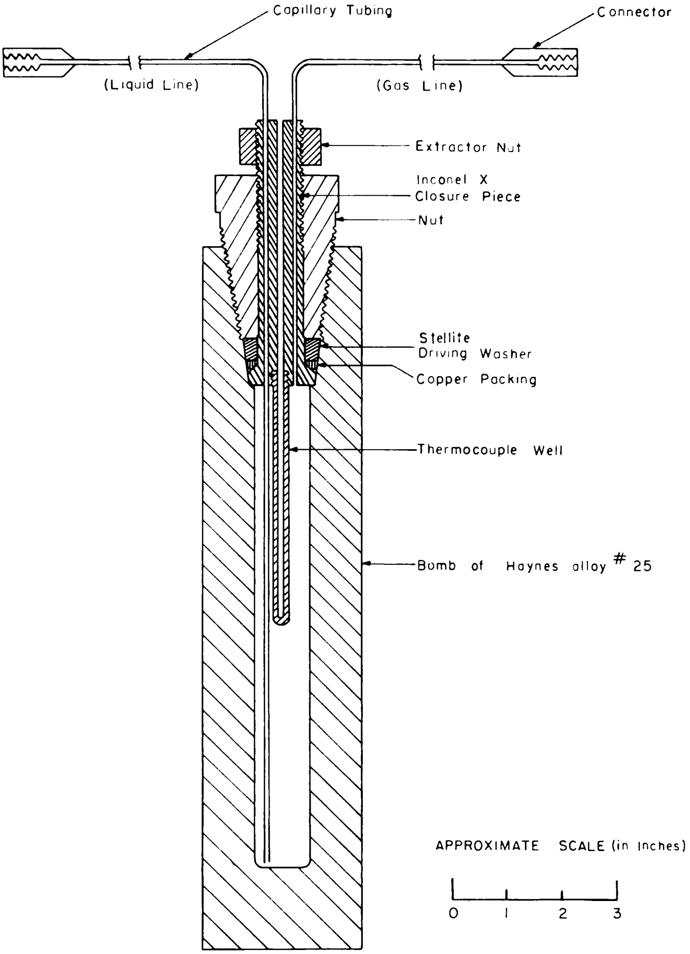

Fig. 7. Details of bomb employed in these experiments.

same region as that studied by Ölander and Liander (1950) have also been presented by Antony and Berkowitz (1958).

The electrical conductivity of supercritical solutions of NaCl and H_2O vapor have been studied by Spillner (1940).

THESE INVESTIGATIONS

We have redetermined the vapor pressure of saturated aqueous sodium chloride solutions over the temperature interval 250°-700°C. These determinations fix the temperatures and pressures of the gas-solid-liquid boundary curve. In addition, we have determined the solubility of solid NaCl steam in the gas-solid equilibrium region through the temperature interval 350°-750°C, at pressures up to saturation pressure. We have also determined the compositions of coexisting gases and liquids up to critical pressures for isotherms ranging from 350°-700°C. The maximum pressure in these investigations was the critical pressure at 700°C, approximately 1240 bars.

APPARATUS

Stellite bombs of Haynes alloy no. 25 were used throughout this investigation. The design of the bombs was similar to those previously employed (Kennedy, 1950). A diagram of the bomb is shown in figure 7. The bomb had a ratio of outside diameter to inside diameter of approximately 3. The effective volume of the bomb was approximately 105 cc. A tapered nut was used to seal the bomb. The nut had eight threads per inch and a taper of three inches per foot. Because of the tapered nut, the bomb can be easily disassembled. A partial turn of the nut immediately releases all threads. The driving washer and nut were made of the same alloy as the bomb. An unsupported area copper packing was used to provide a gas tight closure. The closure piece of the bomb, pierced with three holes, was made of Inconal X. The central hole was fitted with a stainless steel thermocouple sheath. The other holes were fitted with stainless steel capillary tubing of 0.100 inch o.d. and 0.018 inch i.d. One of these capillary tubes extended to the bottom of the bomb and was used to

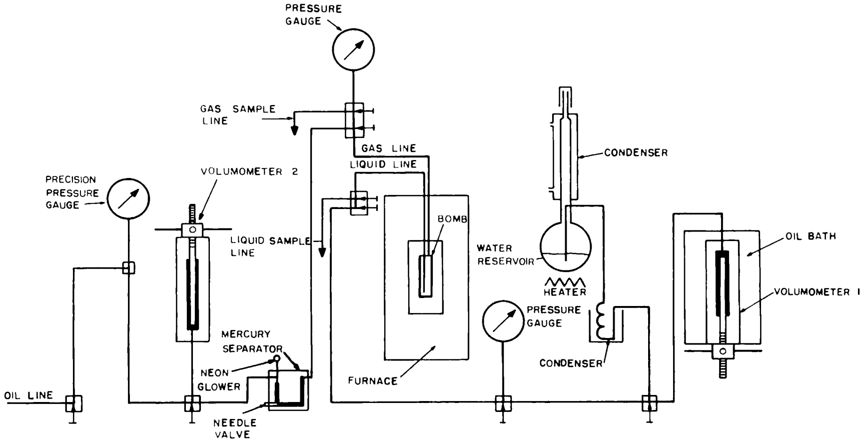

Fig. 8. Schematic diagram of apparatus.

sample liquid. The other capillary tubing extended through the closure piece and was used as a gas sample line. These tubes were welded in place.

The bomb was heated in a furnace of 3 inches inside diameter and 24 inches length. The temperatures were determined by a platinum-platinum 10% rhodium thermocouple and type K potentiometer. The thermocouples were regularly compared against two other thermocouples calibrated at the National Bureau of Standards.

Pressure measurements were made with two 15-inch face diameter Heise Bourdon Tube gauges. These gauges had ranges of 0-500 bars with scale divisions of one-half-bar intervals and 0-1400 bars with scale divisions at two-bar intervals. The gauges were calibrated by comparison against a free piston gauge. Their precision and hysteresis was within less than one scale division.

A schematic diagram of apparatus is shown in figure 8. The bomb was connected to the Heise gauge through the mercury U-block separator and the oil-filled volumometer 2. The surface of the mercury in the U-block was located with a neon glower connected to an insulated needle. The approximate pressure in the bomb was noted from a rough gauge connected directly to the bomb (fig. 8). The piston in volumometer 2 was then advanced until the pressure shown on the Heise gauge was approximately equal to the pressure shown by the rough gauge. The needle was then opened in the mercury U-block so that the pressure on the Heise gauge adjusted to that in the bomb. The piston in volumometer 2 was again adjusted so that the level of the mercury in the U-block barely made contact with the tip of the insulated needle. as shown by the neon glower. The pressure reading on the Heise gauge now showed the exact pressure in the bomb.

MEASUREMENTS OF VAPOR PRESSURE OF SATURATED AQUEOUS SODIUM CHLORIDE SOLUTIONS

Approximately 60 gm of analytical grade sodium chloride were taken into the bomb and the bomb closed and sealed. The bomb was placed in the furnace and the temperature raised to approximately 700°C. Conductivity water from the condenser (fig. 8) was drawn into volumometer 1 and, by appropriate manipulation of the valve, then compressed and forced into the bomb. The water was introduced into the bomb in small increments, allowing about three hours between each increment. The water was introduced until further water did not increase the pressure in the bomb. It was clear at this point that the three-phase boundary line had been encountered with gas-solid-liquid equilibrium. Measurements of vapor pressure versus temperature were made on a cooling curve from 700°-200°C and then repeated on a heating curve in which temperatures ranged from 200°C up to 700°C. A period of at least six hours was allowed for the attainment of equilibrium at each temperature, although after about two hours no further changes in pressure at a given temperature were observed. At least three identical or consistent readings were taken at each temperature and pressure.

The results of these determinations are shown in figure 6. Our data are consistent with the data by Keevil, Ölander, and Liander, and by Morey and Chen shown in figure 5. Our results from the cooling and heating cycle are

Table 1

Vapor pressure of saturated aqueous sodium chloride solutions.

Temperature-pressure data for the gas-solid-liquid boundary curve for the system H_2O–NaCl

Temperature °C	Vapor pressure bars	Temperature °C	Vapor pressure bars	Temperature °C	Vapor pressure bars
707.0	269.5	425.8	222.0	313.2	75.6
668.1	335.5	405.3	190.6	343.5	105.8
609.3	389.5	386.2	161.6	375.0	146.5
600.0	392.0	384.6	160.6	406.8	191.9
577.5	390.0	363.5	131.2	438.8	240.0
558.6	384.0	343.5	106.0	470.0	288.0
555.3	381.5	323.0	84.8	501.9	332.2
527.8	360.0	300.8	66.6	525.0	358.2
504.4	334.5	279.3	52.0	560.0	384.0
502.6	333.5	259.8	38.8	604.3	391.0
488.9	314.5	219.5	21.5	610.0	388.0
466.9	283.0	249.5	33.5	633.9	373.5
465.0	281.0	280.0	51.0	675.0	326.2
446.6	253.0	312.2	75.1	708.5	269.0
444.3	250.5				

shown in table 1. The data obtained from the cooling curve and the heating curve are in excellent agreement.

COMPOSITIONS IN THE GAS-SOLID REGION IN THE SYSTEM H_2O–NaCl

The solubility of the solid NaCl in H_2O vapor has been determined at temperatures ranging from 350°-750°C up to saturation pressures. The following experimental method was employed: Approximately 60 gm of solid analytical grade sodium chloride were introduced into the bomb and the bomb sealed. The bomb was then brought to a desired temperature. Conductivity water was then introduced into the bomb in small increments until saturation pressures were reached. The temperature and pressure of the bomb were recorded immediately before sampling. A sample was then drawn through the gas line connected to the top of the bomb. The gas line was slowly opened and a few bubbles of steam allowed to condense in the gas line and escape, thus rinsing the gas-sampling capillary tube with a sample of the material to be analyzed. A sample of the steam ranging from 0.05-0.15 gm was then slowly drawn into an accurately weighed 25-cc standard volumetric flask about half filled with conductivity water. The difference between the initial and final weight of the volumetric flask gave the exact weight of the sample taken. Pressure drop during the sampling procedure was kept within two bars. After the sample was taken, the temperature and pressure of the system were recorded. The mean of initial and final temperature and pressure readings were recorded as the condition of the steam sample withdrawn from the bomb. In all cases during sampling, the temperature drop was less than 0.5°C. After sampling, the pressure was again brought back to the initial temperature by introducing a small amount of water via volumometer 1. Three hours allowed for equilibrium to be reattained and a second sample drawn. At least two samples were drawn for each temperature and pressure, and the mean value of the sodium chloride dissolved in steam was recorded. At concentrations below one percent NaCl, duplicate runs agreed within a maximum concentration deviation of 8 parts

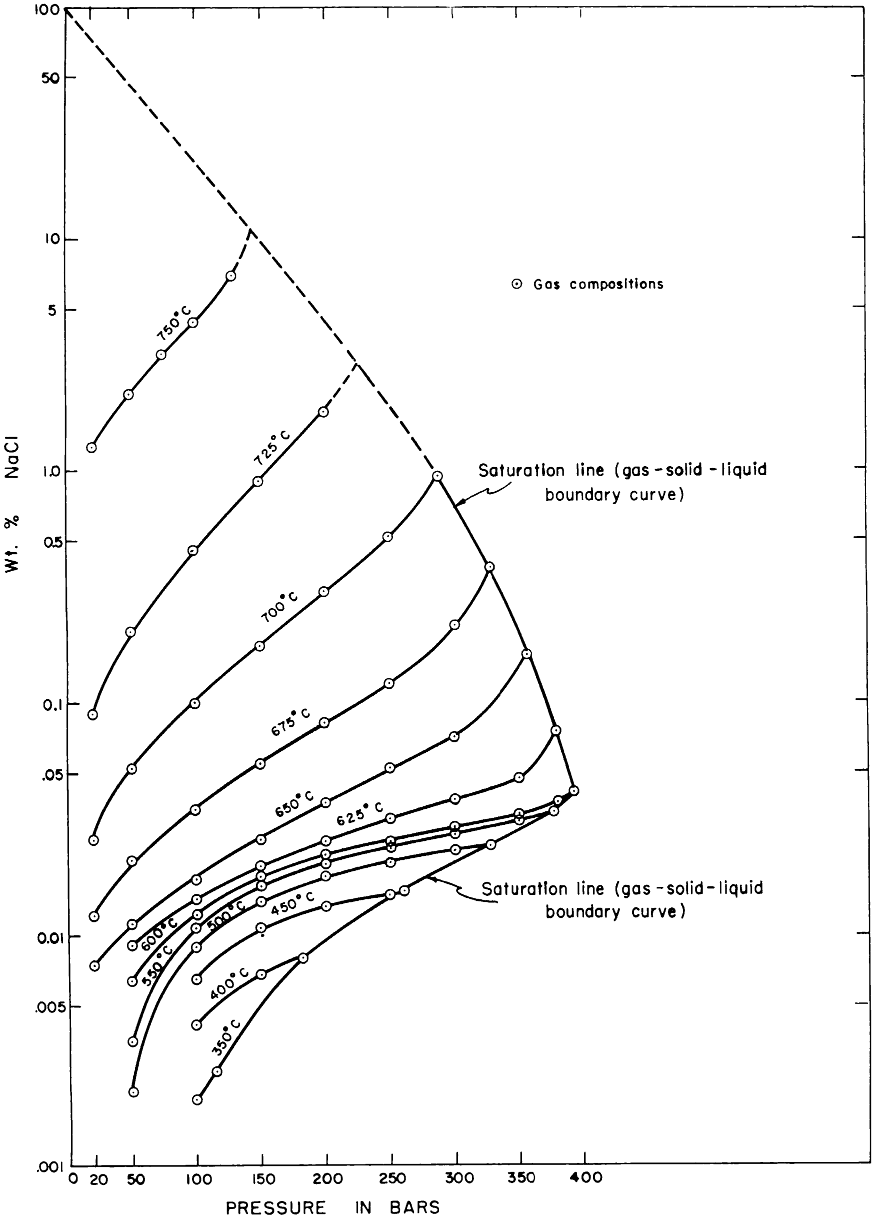

Fig. 9. Isothermal solubility of crystalline NaCl in H_2O at various temperatures and pressures.

per million. It was found convenient to carry out experiments along isotherms from higher pressures to successively lower pressures.

The sample of H_2O + NaCl, extracted from the bomb, was analyzed by the following methods: A supply of conductivity water was made by passing distilled water through the "Bantom Demineralizer". The resulting conductivity water usually contained about 0.03 parts per million of extraneous ions expressed as NaCl. The steam sample drawn from the bomb into the partially filled 25-cc standard flask was first made up to 25 cc. At concentrations below one percent, the NaCl content in the sample of the made-up solution was determined by use of the Beckman Model DU Flame Spectrophotometer. A photomultiplier attachment, used in conjunction with the Flame Spectrophotometer,

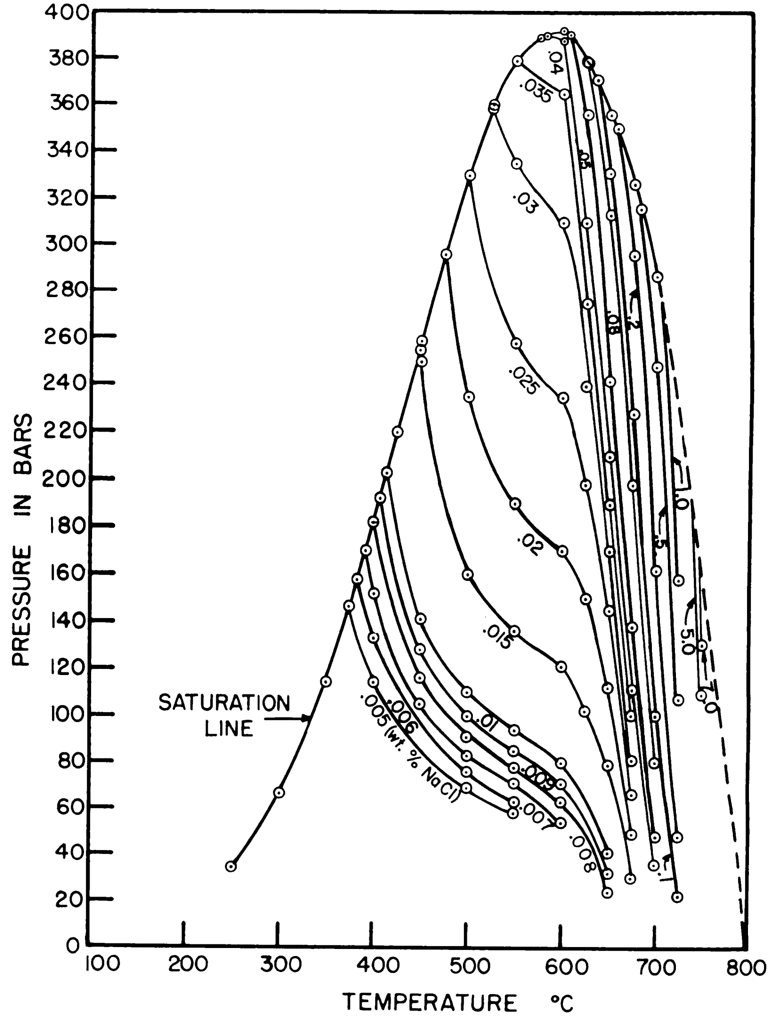

Fig. 10. Isocompositional curves showing solubility of crystalline NaCl in H_2O gas.

increased the flame signal many fold so that very small concentrations of NaCl could be measured accurately. The concentration of NaCl in our unknown samples was determined by comparing the flame signal against signals obtained from a series of standard solutions.

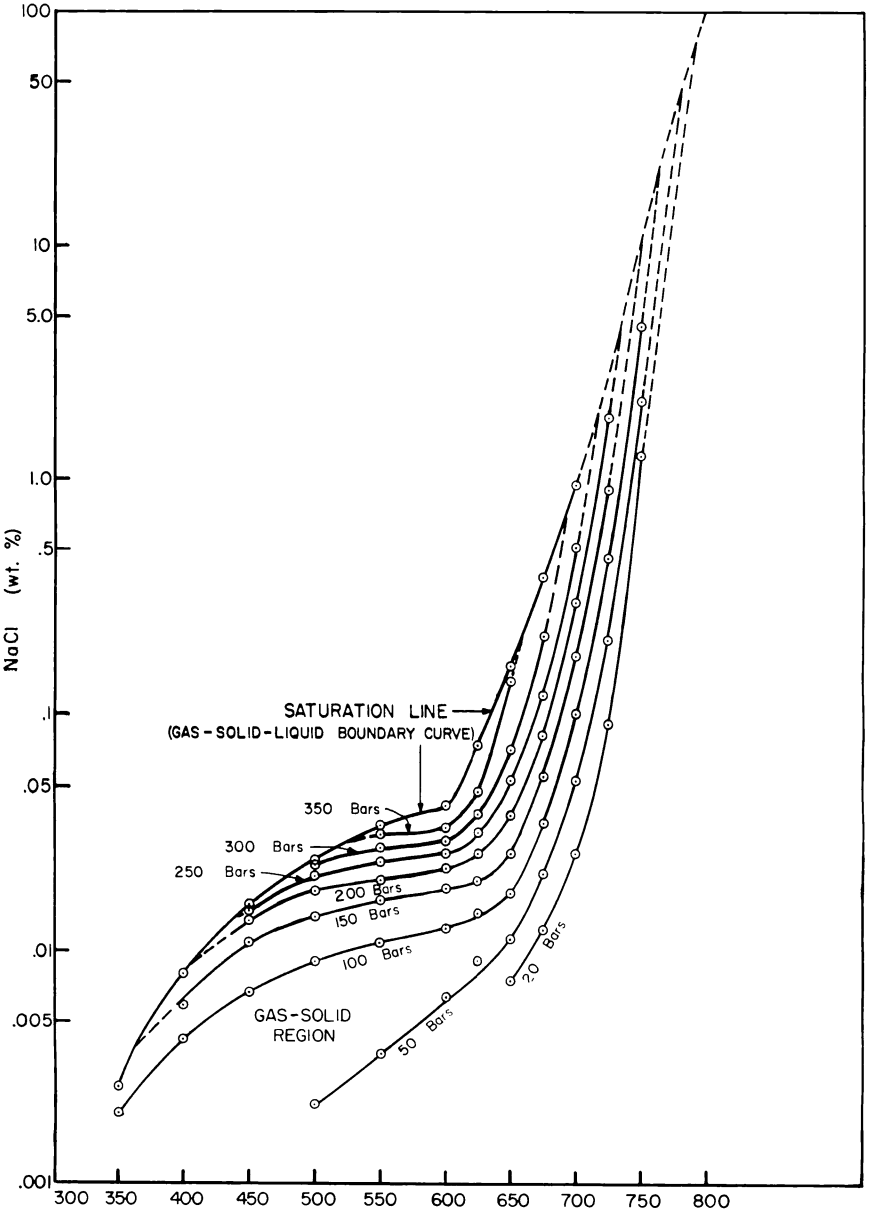

Fig. 11. Isobaric curves showing solubility of crystalline NaCl in H_2O gas.

TABLE 2

Solubility of sodium chloride in steam in the gas-solid equilibrium region for the system H_2O–NaCl

Temperature °C	Pressure bars	Wt percent NaCl in steam
350	114	0.0026*
350	100	0.0020
400	182	0.0080*
400	150	0.0069
400	100	0.0042
450	259	0.0157*
450	250	0.0149
450	200	0.0134
450	150	0.0109
450	100	0.0067
500	330	0.0243*
500	300	0.0234
500	250	0.0209
500	200	0.0180
500	150	0.0140
500	100	0.0090
500	50	0.0022
550	379	0.0343*
550	350	0.0314
550	300	0.0276
550	250	0.0240
550	200	0.0203
550	150	0.0164
550	100	0.0109
550	50	0.0036
600	392	0.0414*
600	380	0.0377
600	350	0.0334
600	300	0.0293
600	250	0.0256
600	200	0.0225
600	150	0.0184
600	100	0.0124
600	50	0.0064
625	379	0.0744*
625	350	0.0472
625	300	0.0382
625	250	0.0319
700	287	0.9416*
700	250	0.5086
700	200	0.3004
700	150	0.1755
700	100	0.1006
700	50	0.0531
700	20	0.0260
725	200	1.8235
725	150	0.9009
725	100	0.4609
725	50	0.2052
725	20	0.0906
750	130	7.015
750	100	4.526
750	75	3.206
750	50	2.155
750	20	1.282
625	200	0.0255
625	150	0.0200
625	100	0.0145
625	50	0.0092
650	356	0.1600*
650	300	0.0712
650	250	0.0527
650	200	0.0376
650	150	0.0260
650	100	0.0178
650	50	0.0112
650	20	0.0075
675	326	0.3815*
675	300	0.2148
675	250	0.1200
675	200	0.0821
675	150	0.0550
675	100	0.0352
675	50	0.0213
675	20	0.0123

* Saturated solution.

* Saturated solution.

All concentrations of NaCl above one percent were determined by Volhard's method of volumetric analysis. The chloride was precipitated with an excess of silver nitrate and the excess silver nitrate back-titrated with standard ammonium thiocyanate (Furman, 1939, p. 271).

Our experimental results of solubility of solid crystalline NaCl in H_2O gas are shown in figures 9, 10, and 11. Figure 9 shows the isothermal solubility of crystalline NaCl in H_2O gas. Figure 10 shows the isocompositional curves of solid NaCl in H_2O gas bounded by the three-phase temperature-pressure-composition line. The isobaric solubility curves are shown in figure 11. Our experimentally determined values for the composition of vapor in the solid-gas region are shown in table 2.

COEXISTING GAS-LIQUID COMPOSITIONS IN THE SYSTEM H_2O–NaCl

A region with two coexisting fluid phases is present at pressures above the melting pressure of crystalline NaCl and below the critical pressure. Measurements of the composition of coexisting fluid phases and of the critical pressure for each isotherm were made as follows: A solution of sodium chloride in water was made up of the approximate critical composition expected for the isotherm to be investigated. Approximately 60-80 cc of this solution were taken into the sealed bomb via the liquid sample capillary line. The bomb was then taken to the required temperature. A sufficient amount of sodium chloride solution was initially introduced into the bomb so that at the isotherm under investigation the initial pressure developed in the bomb was above the critical pressure for the isotherm. Thus, at temperature, initially only one fluid phase existed in the bomb, and the compositions of the samples drawn from the top and the bottom outlets were identical. The pressure in the bomb was then reduced in successively small steps by extracting some of the fluid from the bomb. After each extraction of fluid, and consequent reduction in pressure, samples of the solution were drawn from the bomb through both the top and the bottom capillary outlets. The composition of these samples was determined. As long as the compositions of the two samples remained identical, there was

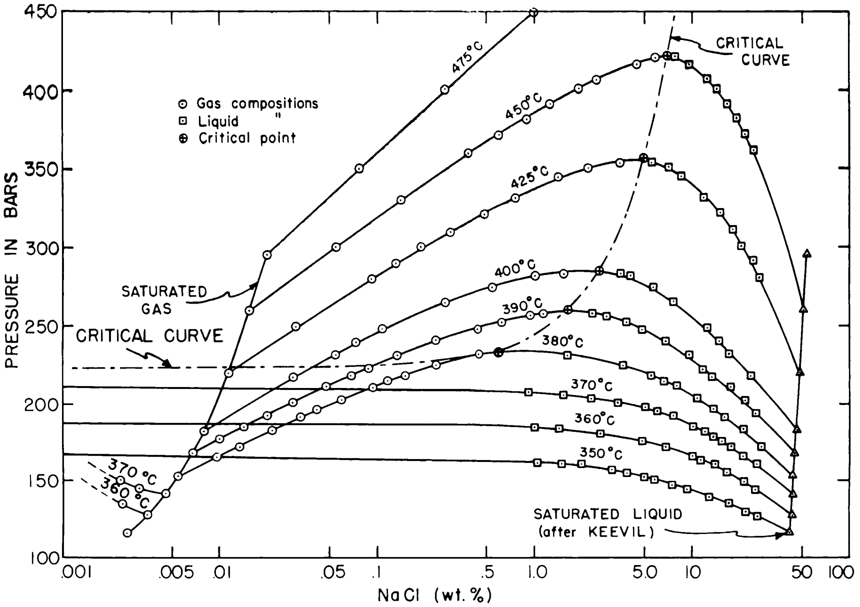

Fig. 12. Isotherms, 350°C-450°C, showing compositions of coexisting gases and liquids,

evidence that only one fluid phase existed in the bomb and that pressures were still supercritical. Eventually, however, a pressure was reached at which two fluid phases appeared, i.e. the sample drawn from the top and the bottom of the bomb showed different compositions. These two fluid phases thus showed the gas and liquid compositions immediately below the critical pressure. The gas and liquid compositions, in equilibrium with each other, were then determined at successively lower pressures along the isotherm down to a pressure approaching the three-phase equilibrium pressure, i.e. the previously determined saturation pressure for gas-solid-liquid equilibrium. A period of one and a half hours was found sufficient for attainment of gas-liquid equilibrium for each pressure. All experiments were made at two- to three-hour intervals. The technique of withdrawing sample and analysis was as previously described. Approximately 0.1-0.2 gm of sample were taken for analysis of both the fluid and gas phases for each pressure. During sampling the total pressure drop was less than two bars, and the temperature drop was less than 0.5°C in all cases.

Isotherms ranging from 350°-700° were studied. The maximum pressure encountered for two-phase equilibrium was at the critical pressure of 1237

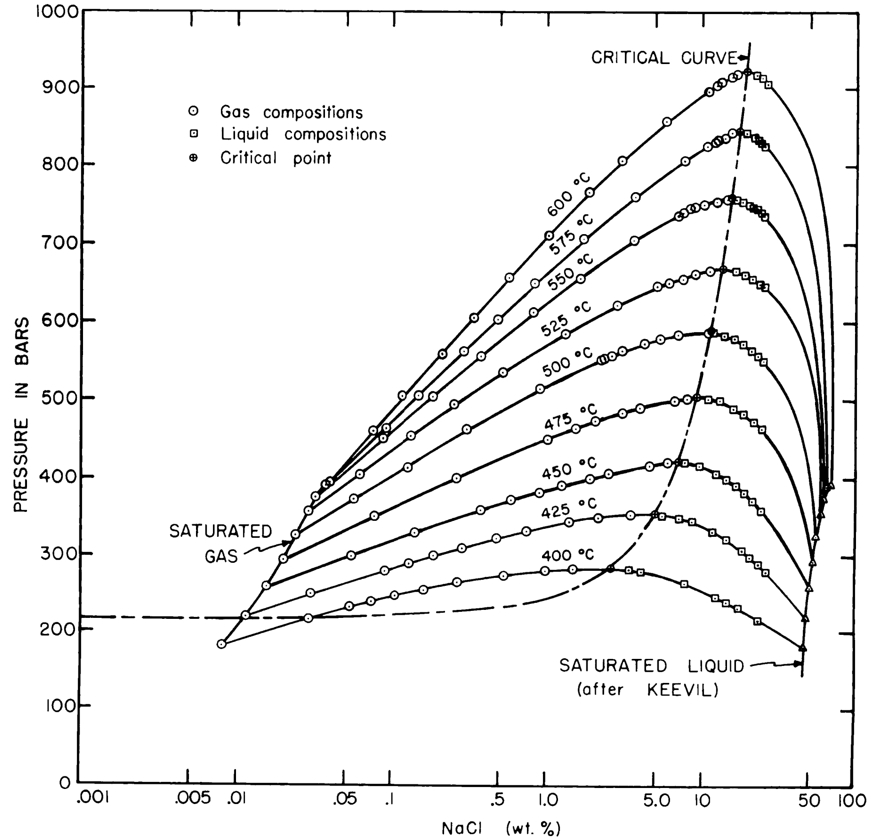

Fig. 13. Isotherms, 400°C-600°C, showing compositions of coexisting gases and liquids.

TABLE 3

Pressure-temperature-composition data in the gas-liquid equilibrium region in the system sodium chloride–water (*Keevil's data)

350°C			360°C		
Pressure bars	Wt percent NaCl in gas phase	Wt percent NaCl in liquid phase	Pressure bars	Wt percent NaCl in gas phase	Wt percent NaCl in liquid phase
165	0	0	187	0	0
162	—	1.040	184	—	1.007
161	—	1.500	183	—	1.426
160	—	2.016	180	—	2.600
157	—	3.110	175	—	4.840
155	—	3.917	172	—	6.820
153	—	4.913	166	—	10.00
151	—	5.762	164	—	11.21
148	—	7.603	160	—	13.90
145	—	9.526	156	—	16.82
140	—	12.96	150	—	21.18
135	—	17.00	145	—	25.46
130	—	21.92	135	0.0024	—
127	—	25.6	127	0.0035	42.25*
114	0.0026	41.5*			(Saturated solution)
		(Saturated solution)			
370°C			**380°C**		
210	0	0	234	0.6	0.6
207	—	0.9128	232	0.4458	1.662
205	—	1.526	225	0.2340	3.706
203	—	2.341	219	0.1498	5.512
200	—	3.348	215	0.1172	6.668
197	—	5.003	211	0.0928	7.950
195	—	6.012	203	0.0600	10.81
191	—	7.622	196	0.0416	13.72
185	—	10.37	191	0.0328	16.53
182	—	12.08	183	0.0217	21.30
179	—	13.42	172	0.0133	27.51
175	—	15.62	165	0.0097	—
172	—	17.91	153	0.0056	44.0*
166	—	21.30			(Saturated solution)
160	—	25.96			
150	0.0024	—			
145	0.0031	—			
140	0.0046	43.1*			
		(Saturated solution)			
390°C			**400°C**		
260	1.66	1.66	285	2.6	2.6
259	1.143	2.305	283	1.510	3.483
257	0.9426	2.889	281	1.000	4.118
253	0.6189	3.856	274	0.5420	5.680
249	0.4318	4.810	265	0.2710	7.820
241	0.2350	6.802	248	0.1070	12.41
231	0.1336	9.717	240	0.0741	14.60
224	0.0882	11.81	232	0.0542	17.14
219	0.0684	13.67	218	0.0296	23.54
211	0.0467	17.12	182	0.0080	46.0*
201	0.0296	21.20			(Saturated solution)
193	0.0203	25.61			
185	0.0142	—			
177	0.0100	—			
167	0.0068	45.0*			
		(Saturated solution)			

TABLE 3 (Continued)

425°C			450°C		
Pressure bars	Wt percent NaCl in gas phase	Wt percent NaCl in liquid phase	Pressure bars	Wt percent NaCl in gas phase	Wt percent NaCl in liquid phase
356	5.0	5.0	422	7.1	7.1
354	3.512	5.610	421	6.021	7.780
350	2.196	7.204	417	4.620	9.656
345	1.432	8.736	407	2.526	12.44
332	0.7640	11.95	400	1.926	14.47
322	0.4810	14.88	391	1.285	16.79
310	0.2902	18.14	382	0.9080	18.99
300	0.1900	20.53	372	0.6000	21.73
290	0.1310	23.51	360	0.3810	24.62
280	0.0920	26.51	330	0.1421	—
250	0.0305	—	300	0.0552	—
220	0.0115	48.5* (Saturated solution)	259	0.0157	51.0* (Saturated solution)

475°C			500°C		
505	9.3	9.3	590	11.5	11.5
504	8.926	9.718	588	11.18	11.70
503	8.012	11.00	583	7.068	13.98
500	6.667	13.03	579	5.423	16.15
490	3.994	15.89	573	4.324	18.51
484	3.101	18.80	565	3.198	21.04
472	2.051	21.54	559	2.651	23.02
464	1.558	24.11	553	2.350	23.92
450	1.012	—	552	2.246	25.06
400	0.2660	—	515	0.9080	—
350	0.0770	—	462	0.3090	—
296	0.0200	53.5* (Saturated solution)	413	0.1280	—
			373	0.0570	—
			330	0.0243	56.1* (Saturated solution)

525°C			550°C		
670	13.6	13.6	760	15.6	15.6
669	13.41	13.72	759	14.86	16.59
667	11.06	16.82	754	12.56	18.12
663	0.120	18.96	750	10.32	20.31
658	7.621	21.20	748	9.170	21.02
654	6.841	22.04	745	8.507	22.91
651	6.092	23.74	740	7.702	23.99
647	5.166	25.61	736	7.081	25.86
622	2.852	—	704	3.652	—
585	1.311	—	658	1.662	—
536	0.5202	—	612	0.8320	—
493	0.2543	—	555	0.3751	—
452	0.1331	—	503	0.1833	—
403	0.0618	—	450	0.0893	—
359	0.0292	59.5* (Saturated solution)	379	0.0342	62.0* (Saturated solution)

TABLE 3 (Continued)

575°C			600°C		
Pressure bars	Wt percent NaCl in		Pressure bars	Wt percent NaCl in	
	gas phase	liquid phase		gas phase	liquid phase
845	17.6	17.6	922	19.6	19.6
842	15.62	19.21	920	18.26	20.85
837	14.03	21.90	918	16.85	22.93
832	12.84	23.08	913	15.72	24.86
830	12.40	23.79	907	13.34	26.82
825	10.92	25.81	902	12.27	—
807	7.706	—	897	11.00	—
760	3.696	—	858	5.962	—
706	1.729	—	806	3.077	—
650	0.8386	—	766	1.896	—
603	0.4821	—	710	1.016	—
561	0.2908	—	656	0.5724	—
505	0.1496	—	603	0.3392	—
464	0.0932	—	559	0.2102	—
389	0.0380	65.0*	503	0.1186	—
		(Saturated solution)	460	0.0761	—
			392	0.0414	69.0* (Saturated solution)

625°C			650°		
1002	21.5	21.5	1082	23.2	23.2
1000	20.32	22.82	1080	21.58	24.50
998	18.61	23.95	1077	18.71	27.46
993	16.76	25.57	1069	15.16	—
983	14.06	—	1061	13.96	—
973	11.98	—	1051	11.82	—
919	5.816	—	1041	10.19	—
862	3.361	—	1031	9.176	—
792	1.790	—	1021	8.210	—
718	0.9663	—	1011	7.387	—
686	0.7521	—	963	4.887	—
630	0.4884	—	911	3.401	—
579	0.3298	—	859	2.356	—
535	0.2375	—	805	1.710	—
484	0.1632	—	750	1.276	—
453	0.1292	—	700	0.9517	—
379	0.0744	72.2*	650	0.7209	—
		(Saturated solution)	602	0.5618	—
			551	0.4348	—
			484	0.3076	—
			430	0.2360	—
			356	0.1600	76.0*

TABLE 3 (Continued)

675°C			700°C		
Pressure bars	Wt percent NaCl in		Pressure bars	Wt percent NaCl in	
	gas phase	liquid phase		gas phase	liquid phase
1163	24.8	24.8	1237	26.4	26.4
1160	21.20	26.44	1234	24.30	—
1157	18.92	—	1228	19.61	—
1145	15.96	—	1218	15.82	—
1131	12.91	—	1210	13.94	—
1113	10.33	—	1200	12.06	—
1097	8.682	—	1192	10.91	—
1087	8.183	—	1180	9.613	—
1072	7.381	—	1170	8.804	—
1059	6.612	—	1150	7.510	—
1045	6.023	—	1132	6.631	—
1033	5.632	—	1108	5.810	—
1017	5.100	—	1078	5.048	—
997	4.613	—	1050	4.500	—
977	4.150	—	1030	4.182	—
959	3.801	—	1000	3.810	—
939	3.501	—	970	3.480	—
927	3.306	—	940	3.200	—
915	3.151	—	910	2.930	—
903	3.004	—	860	2.596	—
858	2.500	—	810	2.331	—
797	1.988	—	758	2.103	—
750	1.698	—	705	1.901	—
702	1.427	—	657	1.720	—
649	1.180	—	604	1.567	—
591	0.9610	—	504	1.313	—
525	0.7570	—	403	1.120	—
464	0.6190	—	287	0.9416	84.0* (Saturated solution)
326	0.3815	80.0* (Saturated solution)			

TABLE 4

Sodium chloride–water system critical temperature-pressure-composition data

Critical temperature °C	Critical pressure bars	Critical composition wt percent NaCl
374	221	0
380	234	0.6
390	260	1.7
400	285	2.6
425	356	5.0
450	422	7.1
475	505	9.3
500	590	11.5
525	670	13.6
550	760	15.6
575	845	17.6
600	922	19.6
625	1002	21.5
650	1082	23.2
675	1163	24.8
700	1237	26.4

bars at 700°C. Unfortunately, no NaCl solubility much above 25 percent could be determined with this apparatus. At concentrations above 25 percent, crystals of NaCl precipitated out and blocked the sampling capillary line.

The compositions of coexisting gases and liquids for 18 isotherms have been determined. These isotherms are shown in figures 12, 13, and 14. These isotherms are terminated by saturated gas and saturated liquid. In all cases we have used Keevil's value for the composition of the saturated liquid, and in figures 12, 13, and 14, the branch of the curve trending toward saturated liquid has been sketched in, using Keevil's data for saturated liquid. The experimentally determined compositions of coexisting phases for each tempera-

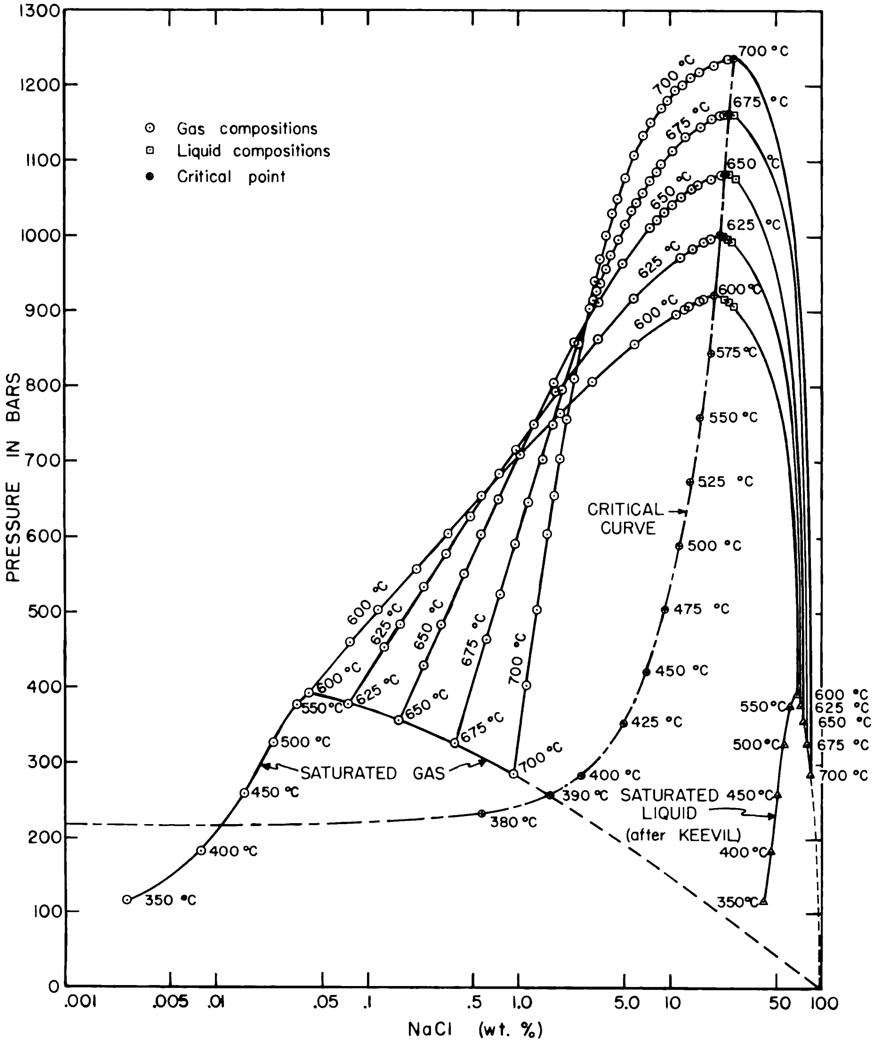

Fig. 14. Isotherms, 600°C-700°C, showing compositions of coexisting gases and liquids.

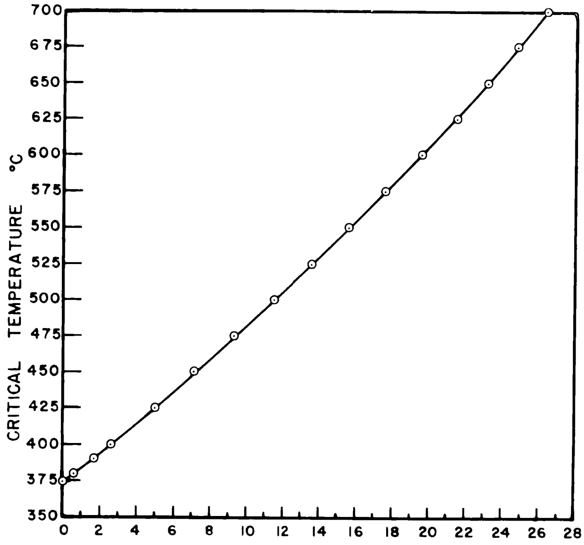

Fig. 15. Critical temperatures of unsaturated aqueous sodium chloride solutions.

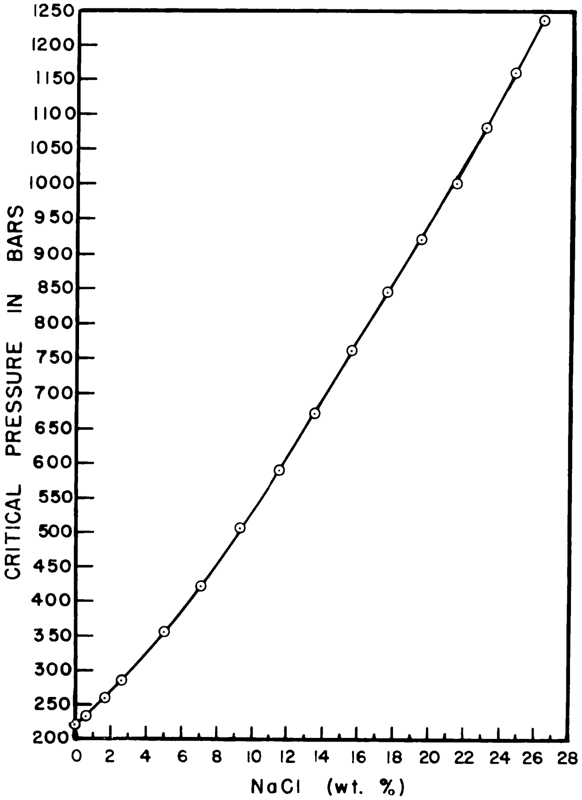

Fig. 16. Critical pressures of unsaturated aqueous sodium chloride solutions.

ture investigated are shown in table 3. For every isotherm, the last entry in the column marked "liquid phase" is the composition of the saturated liquid as taken from Keevil. The composition of the saturated gas is from this work. The distribution of critical temperatures and pressures is shown in figures 12, 13, and 14. Our determined values for critical pressure and critical composition for the various isotherms are shown in table 4. Critical temperatures, pressures, and compositions in the system H_2O–NaCl are plotted in figures 15 and 16. Critical compositions are surprisingly linear with temperature and pressure throughout the studied portion of this system. A crude extrapolation of the curve relating critical composition to critical temperature suggests that the critical temperature of pure NaCl should be approximately 1900°C with a critical pressure of roughly 9.8 bars.

All our data on the system H_2O–NaCl are shown in the three-dimensional diagram, figure 17, where pressure, temperature, and composition are related. Figure 17 shows compositions of gas in equilibrium with solid, the melting surface with coexisting gases, liquids, and solids, the envelope of curves relat-

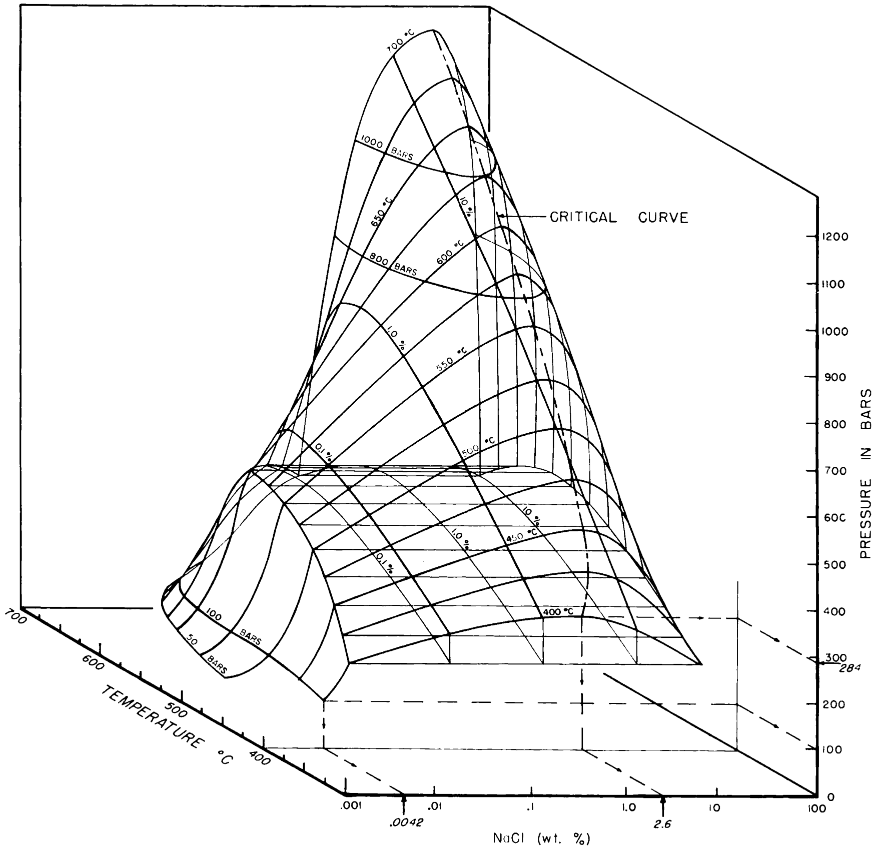

Fig. 17. Temperature-pressure-composition model of the system H_2O–NaCl.

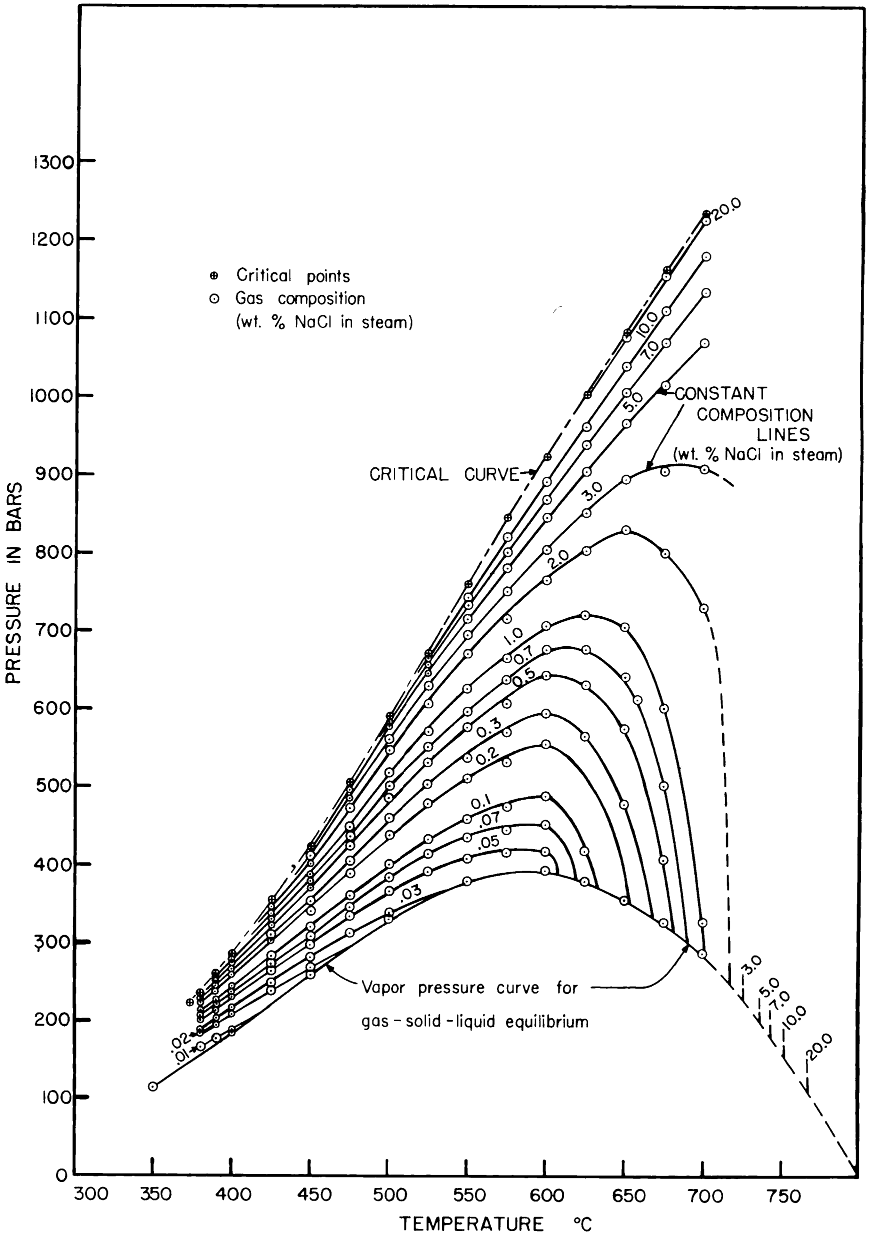

Fig. 18. Isocompositional curves in the gas-liquid region in the system H_2O–NaCl.

ing the composition of the two fluid phases, and the critical composition and pressure for each temperature studied. Isocompositional and isobaric curves in the gas-liquid region are shown in figures 18 and 19.

It would have been highly desirable throughout these experiments to determine the densities of gases and liquids as well as the densities of the fluid at the critical point for each isotherm. Unfortunately, these measurements have not yet been made, and without them it is almost impossible to make any remarks about association or dissociation in this system at high temperatures and pressures. Certain surprising changes in slope of various curves may be noted. In particular, the composition of gas in equilibrium with solid, as shown in figures 9, 10, and 11, is marked by rather abrupt changes in slope at approximately 600°C. This temperature corresponds to the temperature of maximum pressure on the three-phase surface. No simple picture relating solubility in the

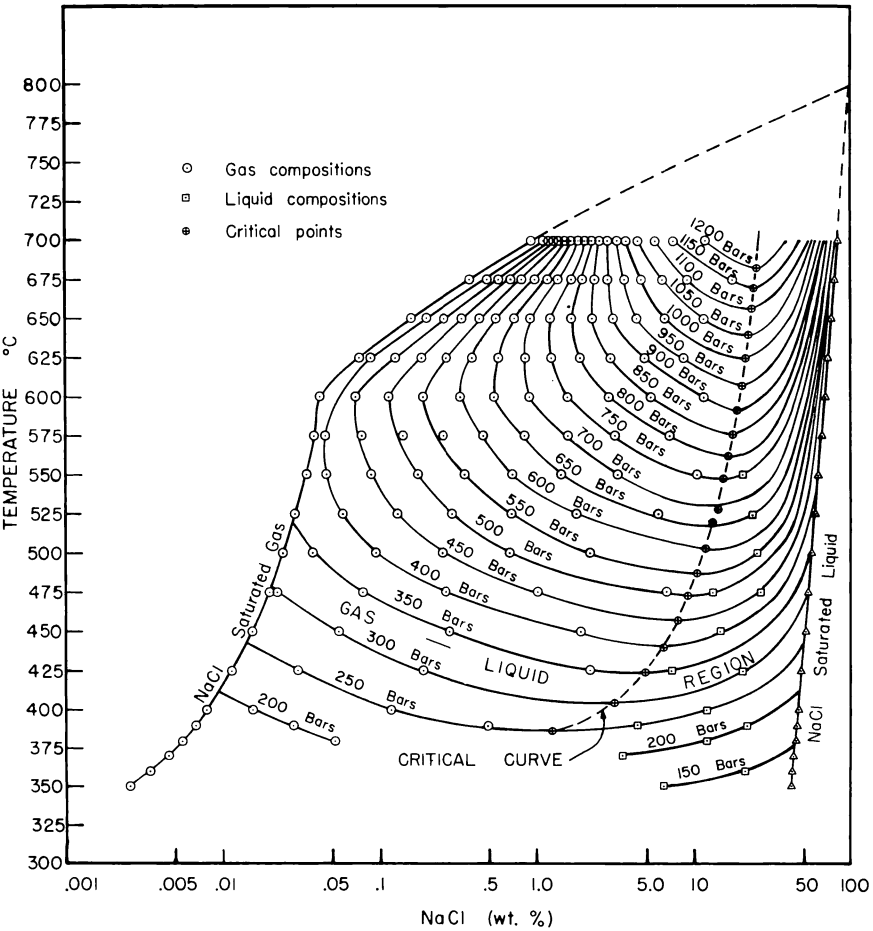

Fig. 19. Isobaric curves in the gas-liquid region in the system H_2O–NaCl.

gas phase to specific volume of water may be seen, as was shown by the system H_2O–SiO_2 (Kennedy, 1950).

IMPLICATIONS OF THE SYSTEM H_2O–NaCl TO THE PROBLEM OF THE ORIGIN OF THERMAL WATERS AND HOT SPRINGS

The problem of the origin of sodium chloride waters in hot springs has been extensively discussed by White (1957). White points out that the alkali ratios of most, if not all, sodium chloride springs suggest that the halogens have been transported as alkali halides dissolved in the magmatic vapor phase. The hot springs rich in sodium chloride, as tabulated by White (1957), contain up to 2500 parts per million sodium chloride. Reference to figure 9 of this paper shows that no severe limitations on the magmatic mechanism are placed by these concentrations of sodium chloride. At pressures of 200 bars and temperatures of 725°C, reasonable pressures and temperatures for the separation of gases from shallow seated magmatic intrusions, escaping supercritical water can contain up to approximately 3 percent NaCl. This is sufficient NaCl to account for even the most saline of White's hot springs and still allows the dilution of magmatic emanations with meteoritic water by as much as ten-fold.

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