# Liquid-vapor relations in the critical region of the system NaCl-H₂O from 380 to 415°C: A refined determination of the critical point and two-phase boundary of seawater

JAMES L. BISCHOFF and ROBERT J. ROSENBAUER

U.S. Geological Survey, Menlo Park, CA 94025, U.S.A.

**Abstract**—Pressure-temperature-composition (*P-T-x*) relations for coexisting vapor and liquid phases in the system NaCl-H₂O were determined experimentally in the critical region from 380 to 415°C. The results provide much improved control on the *P-T-x* critical line in this region. The critical point of seawater (3.2 wt% NaCl solution), which is bracketed in the present study, is at 407°C and 298.5 bar. In addition, the *P-T* two-phase boundary of seawater was re-determined. These results provide increased precision and accuracy for theoretical models of critical phenomena in this important two-component system and of the limiting *P-T* conditions of seawater in seafloor geothermal systems.

## INTRODUCTION

TWO COMPONENT SYSTEMS close to the *P-T-x* (pressure-temperature-composition) critical line display unusual physical and chemical properties. Accumulating evidence suggests that seawater (analogous to 3.2 wt% NaCl solution) may be circulating within the critical region in the subsurface of seafloor geothermal systems. Therefore, accurate knowledge of the critical point and the two-phase boundary of seawater is important. Because natural seawater (average total salinity of 3.7 wt%) loses most of its dissolved SO₄ and Mg during heating above 300°C, its high-temperature analogue is a 3.2 wt% NaCl solution. An earlier work (BISCHOFF and ROSENBAUER, 1984) reported on the experimental determination of the *P-T* two phase boundary of 3.2 wt% NaCl in which experimental uncertainties were on the order of three bars for a given temperature in the range of 200 to 500°C. The critical point lies on this boundary and defines the transition from the boiling curve to the dew-point curve. In this earlier work, the critical point was estimated by the point of inflection on the two-phase boundary, but the uncertainty of this derived critical point (403°–406°C, 285–302 bar) is large, due to the broad region of inflection.

A precisely measured critical point would enable the physical and thermochemical properties of seawater previously described by an empirical equation (BISCHOFF and ROSENBAUER, 1985) to be described by theoretically-based equations in reduced variables (*i.e.*, HAAR *et al.*, 1984). Also, precise information on the critical region of NaCl-H₂O near the critical temperature of pure water is of great importance in the development of theoretical models for this system in the two-phase region (LEVELT-SENGERS *et al.*, 1986; PITZER *et al.*, 1987, PITZER, 1986).

We report here on a series of isothermal experiments providing precise *P-x* control in the critical region for four isotherms bracketing the critical temperature of seawater. The objective was to define the *P-T-x* critical line in the region bracketing 3.2 wt% NaCl, thereby allowing the determination of the seawater critical pressure and temperature by interpolation along this line. Additional experiments were carried out to provide improved control on the *P-T* two-phase boundary of seawater from 200°C to 500°C. In a more general sense the present study provides additional data and control on the critical line and the shape of the two-phase surface in

the *P-T-x* critical region, and is a continuation of earlier studies on the system NaCl-H₂O in an attempt to fill in data gaps and to resolve areas of disagreement in the literature on the two-phase surface of this very important system (BISCHOFF and PITZER, 1985; BISCHOFF *et al.*, 1986; ROSENBAUER and BISCHOFF, 1987; PITZER *et al.*, 1987). Because of greater accuracy, data presented in the present study supersedes experimental data on the *P-T* two-phase boundary presented in BISCHOFF and ROSENBAUER (1985) and the *P-x* critical region of the 380°C isotherm presented in PITZER *et al.* (1987).

## METHOD

The approach for determining the critical point of 3.2 wt% NaCl was to measure points on the *P-T-x* critical line that bracket the composition of interest. Of the three variables, temperature is the most convenient to control. Therefore, isotherms were constructed that defined the vapor-liquid boundary in the critical region at 380°, 400°, 405°, and 415°C that spanned 3.2 wt% NaCl. The critical point for each of these isotherms were then determined graphically and a critical line constructed. This is essentially the same technique used earlier to determine critical points on isotherms between 450° and 500°C (ROSENBAUER and BISCHOFF, 1987). In addition, the two-phase boundary for seawater (3.2 wt% NaCl) was determined between 200° and 450°C with improved accuracy.

In the temperature range of interest, estimates of critical points in the system NaCl-H₂O have been provided by SCHRÖER (1927), SOURIRAJAN and KENNEDY (1962), ÖLANDER and LIANDER (1950), KHAIBULLIN and BORISOV (1966), and MARSHALL and JONES (1974). Considerable disagreement exists among these studies. Except for SCHRÖER (1927) and MARSHALL and JONES (1974), who used optical techniques, critical points were estimated from the shape of individual isotherms. Presumably, although this was not specified, the critical points were estimated by projecting experimentally determined points from both the vapor and liquid limbs of isotherms in *P-x* coordinates to the apex (point of maximum pressure). The top of the isotherms are particularly broad at these temperatures and only few points on the limbs were determined experimentally, and these mostly far from the critical point. Therefore, such projections, although fairly accurate for determining the critical pressure, will have large errors associated with estimates of critical composition. The approach of the present study was to determine a large number of points within the critical region of a group of isotherms, in order to maximize control on the geometry and projection to the critical pressure and composition.

## EXPERIMENTAL TECHNIQUES

Procedures were essentially those used earlier (ROSENBAUER and BISCHOFF, 1987) with some modifications. We employed a constant volume (26 ml working volume) pressure vessel made of passivated

Table 1. Experimentally determined points on two-phase boundary of seawater. Pressures are for start and end of sample during which phase separation took place.

| T (°C) | P (bars) | |
|---|---|---|
| | Start | End |
| 195.6 | 14.1 | 14.1 |
| 251.9 | 40.7 | 40.7 |
| 299.6 | 83.5 | 83.4 |
| 309.5 | 95.9 | 95.8 |
| 319.6 | 109.6 | 109.4 |
| 350.1 | 161.0 | 160.8 |
| 370.2 | 203.6 | 203.4 |
| 390.2 | 253.8 | 253.7 |
| 400.2 | 280.2 | 279.7 |
| 405.2 | 293.4 | 292.8 |
| 409.8 | 305.4 | 304.8 |
| 415.2 | 319.8 | 319.3 |
| 429.4 | 358.2 | 357.2 |
| 449.8 | 411.5 | 409.7 |

René 41 alloy[1]. Separate capillary tubes and valves permit independent sampling of the vapor phase from the top, and of the liquid through a dip tube from the bottom of the vessel. An improvement over previous applications was the insertion of inconel wire into the capillary tubes to decrease the inner volume of the capillary. The diameter of the wire (0.635 mm) was only slightly less than the inner diameter of the capillary (0.686 mm), thereby radically decreasing the dead volume (the amount of fluid required during sampling to flush the lines). Therefore, the pressure drop between the beginning and end of sampling was greatly reduced. This pressure interval represents the pressure uncertainty of the position of the two-phase boundary for any given experiment. Pressure intervals at the point of phase separation are reduced to about 0.75 bars compared to about 1 to 3 bars in earlier studies (i.e. BISCHOFF and ROSENBAUER, 1984). René 41 is non-corrosive with respect to salinities and temperatures of up to at least 25 wt% NaCl and 500°C, as indicated by the lack of detectable evolved $H_2$ (<0.5 mmol/Kg) in the vapor. The vessel was maintained within a fluidized particle-bath furnace and temperature monitored by two ⅛ inch-diameter inconel-sheathed Pt-resistance thermometers (100 Ohm RTD), one placed in the head of the vessel and the other at the base. Each RTD is individually calibrated at multiple temperatures against standards that are traceable to the National Bureau of Standards (NBS) and are in accordance with the International Practical Temperature Scale of 1968 (IPTS-68). Calibrated accuracies are ±0.27° at 200°C, ±0.40° at 300°C and ±0.14° at 400°C. These accuracy values represent maximum errors due to the combined effects of sensor hysteresis and repeatability, and calibration equipment inaccuracies. The calibrated sensor constants are programmed directly into a digital temperature indicator. Instrument error is negligible at ±0.026°C maximum. Vertical temperature gradients were minimized by varying the degree of fluidization until the temperature of the top and bottom agreed within 0.2°C. Pressure was monitored by two parallel-mounted transducers: one a Serta Systems model 300C, 0 to 689.6 bar range, accurate to ±0.3 bar, and the other a Sensotec model TJE, 0 to 1034.5 bar range, accurate to ±0.5 bar. Both units were calibrated by dead weights to their stated accuracies. Fluid samples (0.2 ml) were analyzed for chloride by a Radiometer/Copenhagen model cmt 10 chloride titrator, with a relative precision of 0.5% for samples containing more than 1.0 wt% NaCl, and 2% for those below 1 wt% NaCl.

All experiments began in the single phase region at a pressure approximately 50 bars above the two-phase boundary. Samples of 0.2 mls were taken sequentially from either the top or the bottom of the vessel to decompress the system until the point of phase separation. The phase boundary was recognized by a change in salinity within a single sample, and the pressure interval for that sample noted. A change in the relative drop in pressure per sample weight was also noted at the phase boundary. In the case of the P-T two-phase boundary for seawater, the vessel was filled with 3.2 wt% NaCl, and 14 experiments were conducted from 195° to 450°C. Each of these experiments was terminated at the point of initial phase separation.

Table 2. Coefficients for the equation

$$P \text{ (bars)} = \sum_{i=0}^{7} c_i T^i$$

describing vapor pressures of vapor-saturated seawater (3.2 wt% NaCl solution) as a function of T (°C) from 200° to 500°C. Data from Table 1 with additional points for 450°, 475°, and 500°C taken from Rosenbauer and Bischoff (1987).

$c_0 = -3.14653 \times 10^3$
$c_1 = +8.418717 \times 10^1$
$c_2 = -9.37853678 \times 10^{-1}$
$c_3 = +5.6426562 \times 10^{-3}$
$c_4 = -1.97983687 \times 10^{-5}$
$c_5 = +4.05569695 \times 10^{-8}$
$c_6 = -4.4790140 \times 10^{-11}$
$c_7 = +2.0551959 \times 10^{-14}$

In the case of the P-x isotherms, experiments were conducted at 380.0°, 400.2°, 405.2° and 415.2°C, and at many different compositions for each isotherm. In these experiments, sampling was carried out to the point of phase separation and was continued until exhaustion of the charge, which provided data on the two-phase boundary away from the critical point on either the vapor or liquid limb of the isotherm of interest. Each sample in this procedure (10 samples in a typical experiment) is not a single pressure-composition point but rather an integration of compositional change over a finite pressure drop. The pressure drop is minimized by the small dead volume employed in the present study. Multiple experiments, each with a different starting salt content, were required to define the isotherm with overlapping segments from different experiments along both liquid and vapor limbs. A difficulty in conducting these multiple experiments on a single isotherm was reestablishing the same temperature in successive experiments. In the critical region, it was necessary to conduct successive experiments within 0.2°C.

Besides the stated uncertainties in measurement of temperature, pressure, and weight-percent NaCl, two additional sources of error might affect the results. During an 8-hour period the temperature of the vessel slowly cycles over a span of about one degree. Sampling was forestalled until the thermometers read within 0.2° of the temperature of interest and 0.2° of each other. There might be slight but unassessable thermal lags during such cycling between the temperature of the charge and the temperatures read by the thermometers. The other source of error is the sluggishness of phase separation close to the critical point. Differences in physical properties and chemical potential of the two phases are diminishingly small as the critical point is approached. Therefore, the actual observance of phase separation is at some pressure finitely below the phase boundary. Because

Table 3. Temperature, pressure, and specific volume of vapor-saturated seawater (3.2 wt% NaCl solution). Pressure calculated from polynomial of Table 2 for a given temperature. Specific volume (V) calculated from Bischoff and Rosenbauer (1985).

| T° (C) | P (bars) | V (cc/g) |
|---|---|---|
| 200 | 15.3 | 1.14 |
| 210 | 18.6 | 1.15 |
| 220 | 22.6 | 1.17 |
| 230 | 27.4 | 1.18 |
| 240 | 32.9 | 1.20 |
| 250 | 39.2 | 1.22 |
| 260 | 46.3 | 1.24 |
| 270 | 54.2 | 1.26 |
| 280 | 63.0 | 1.28 |
| 290 | 72.9 | 1.31 |
| 300 | 83.9 | 1.34 |
| 310 | 96.2 | 1.37 |
| 320 | 109.9 | 1.40 |
| 330 | 125.3 | 1.45 |
| 340 | 142.3 | 1.50 |
| 350 | 161.1 | 1.56 |
| 360 | 181.7 | 1.63 |
| 370 | 203.9 | 1.72 |
| 380 | 227.4 | 1.87 |
| 390 | 252.7 | 2.19 |
| 400 | 278.8 | 2.48 |
| 410 | 305.6 | 2.71 |
| 420 | 332.6 | 2.86 |
| 430 | 359.6 | 2.96 |
| 440 | 386.3 | 3.03 |
| 450 | 412.2 | 3.07 |
| 460 | 437.4 | --- |
| 470 | 462.1 | --- |
| 480 | 486.5 | --- |
| 490 | 511.7 | --- |
| 500 | 539.1 | --- |

[1] Any use of trademarks is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.
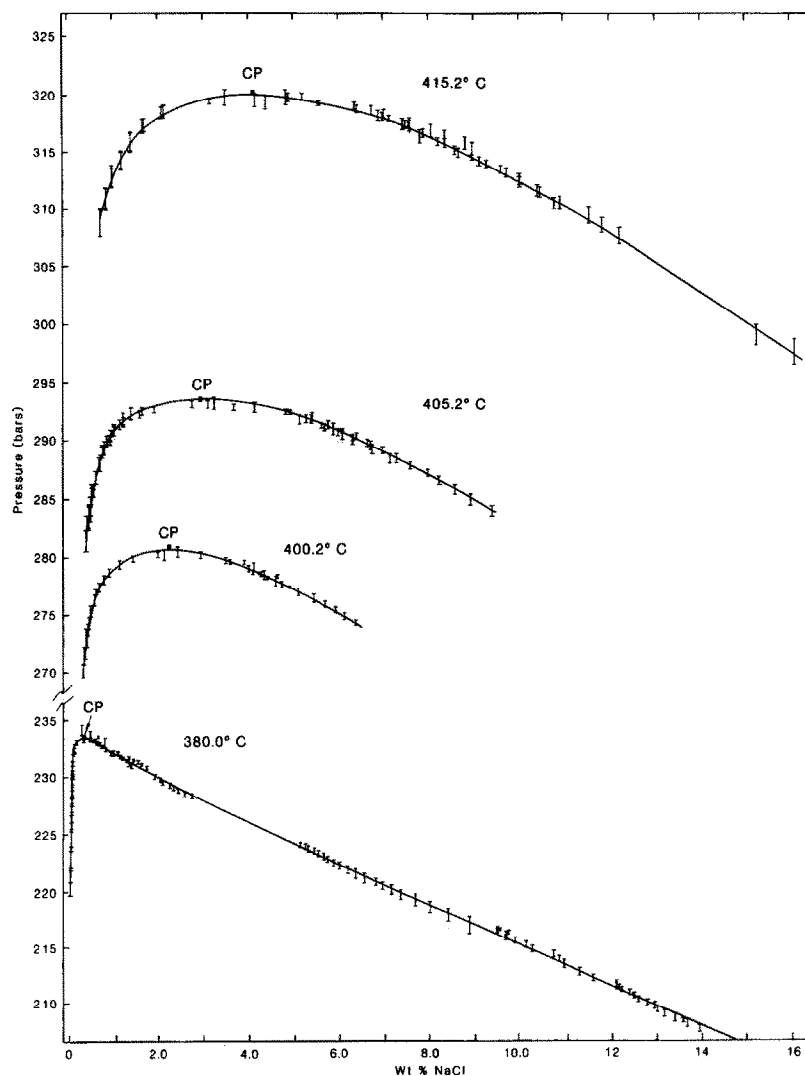
FIG. 1. Experimental results for the vapor-liquid boundary in the critical region from 380 to 415°C for the binary system NaCl-H$_2$O. Experimental pressure and composition points are shown on isothermal plots. Error bars denote the pressures before and after sampling. Left side of each isotherm describes vapor composition and right side describes liquid. CP is the critical point. Above each isotherm is the single-fluid phase region. Horizontal tie-lines (constant pressure) describes composition of coexisting liquid and vapor pairs in the two-phase region.

of the thermal cycling it was not possible to allow more than 10 minutes between successive samples taken during a single experiment. Based on successive experiments within the critical region of each isotherm, points of phase separation in the critical region may be too low by as much as 1.5 bar. For this region, the actual P-x critical point for each isotherm was estimated by graphical projection from the liquid and vapor legs where the boundary is better controlled.

## RESULTS

For the P-T two-phase boundary of 3.2 wt% NaCl, experiments were conducted from 195.6° to 449.8°C, providing 14 points on the boundary. Results (Table 1) show that the pressure uncertainty of the boundary ranges from less than 0.1 bar at the lower temperatures to about 1.8 bars at the higher temperatures. Additional points for 450°, 475° and 500°C were taken from ROSENBAUER and BISCHOFF (1987) and all the data were regressed to a best fit polynomial expression of the pressure of phase separation as a 7th order expansion in temperature:

$$P(bars) = \sum_{i=0}^{7} C_i T^i. \tag{1}$$

The temperature coefficients, $C_i$ are given in Table 1. Pressures calculated from this polynomial expression fit the experimental data (midpoints of range) within an average error of 0.3 bar (maximum error, 0.7 bar at 380°C). Table 3 shows P, T, and specific volume of 3.2 wt% NaCl at the point of phase separation for increments of 10 degrees from 200° to 500°C. For a given temperature, pressure was calculated from the polynomial in Table 2, and specific volume for the given temperature and pressure pair from the equation of state for single-phase seawater (BISCHOFF and ROSENBAUER, 1985).

P-T-x relations in the critical region of the binary system NaCl-H$_2$O from 380 to 415°C are shown in Fig. 1. Each isotherm represents the NaCl content of co-existing vapor and liquid at each pressure. The apex of each isotherm represents the critical point at which the properties of the vapor

and liquid become identical. Sharp asymetry is seen for the 380° isotherm, but this asymetry gradually lessens at the higher temperatures. Increased scatter and uncertainty is shown by experimental points close to the critical point in each of the isotherms reflecting the sluggishness of phase separation in this region.

## DISCUSSION

The critical pressure of each isotherm is determined from the relationship

$$x_l - x_v = \text{const.}(P_c - P)^\beta \qquad (2)$$

where $x_l$ and $x_v$ are the mole fractions of NaCl in the coexisting liquid and vapor phases respectively at pressure $P$, and $P_c$ is the critical pressure. According to classical theory, $\beta = \frac{1}{2}$ (PITZER et al., 1987). Thus, a plot of the difference squared of mole-fraction NaCl of the vapor and liquid, $(x_l - x_v)^2$, versus $P$ projects to $P_c$ as the difference squared approaches zero. Such projections are shown in Fig. 2. Uncertainties of
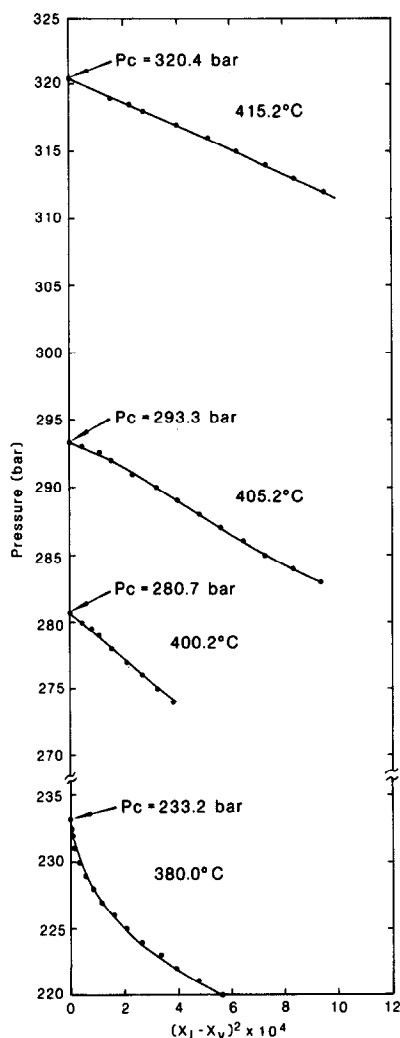


FIG. 2. Critical pressure ($P_c$) determination by projection of the square of the difference between mole-fraction NaCl ($x$) in co-existing liquid ($x_l$) and vapor ($x_v$) for each isotherm from Fig. 1.

Table 4. Pressure and NaCl content of co-existing liquids and vapors in the critical region from 380° to 415°C.

| P(bars) | 380.0°C wt%NaCl vapor | 380.0°C wt%NaCl liquid | P(bars) | 400.2°C wt%NaCl vapor | 400.2°C wt%NaCl liquid |
|---|---|---|---|---|---|
| *233.2±0.2 | 0.35±0.075 | (0.1)** | *280.7±0.15 | 2.22±0.05 | (0.10) |
| 232.5 | 0.140 | 0.84 | 280 | 1.35 | 3.45 |
| 232 | 0.125 | 1.05 | 279.5 | 1.10 | 3.90 |
| 231 | 0.110 | 1.50 | 279 | 0.95 | 4.20 |
| 230 | 0.100 | 1.95 | 278 | 0.80 | 4.70 |
| 229 | 0.091 | 2.50 | 277 | 0.70 | 5.25 |
| 228 | 0.083 | 3.00 | 276 | 0.60 | 5.70 |
| 227 | 0.078 | 3.50 | 275 | 0.52 | 6.15 |
| 226 | 0.075 | 4.05 | 274 | 0.45 | 6.55 |
| 225 | 0.070 | 4.55 | | | |
| 224 | 0.066 | 5.16 | | | |
| 223 | 0.061 | 5.75 | | | |
| 222 | 0.059 | 6.25 | | | |
| 221 | 0.057 | 6.80 | | | |
| 220 | 0.055 | 7.40 | | | |
| 218 | | 8.62 | | | |
| 216 | | 9.50 | | | |
| 214 | | 10.90 | | | |
| 212 | | 12.00 | | | |
| 210 | | 13.18 | | | |

| P(bars) | 405.2°C wt%NaCl vapor | 405.2°C wt%NaCl liquid | P(bars) | 415.2°C wt%NaCl vapor | 415.2°C wt%NaCl liquid |
|---|---|---|---|---|---|
| *293.3±0.3 | 2.96±0.04 | (0.13) | *320.4±0.2 | 4.11±0.04 | (0.27) |
| 293 | 2.00 | 4.15 | 319 | 2.40 | 6.20 |
| 292.5 | 1.55 | 4.75 | 318.5 | 2.13 | 6.70 |
| 292 | 1.35 | 5.20 | 318 | 2.0 | 7.07 |
| 291 | 1.10 | 5.85 | 317 | 1.64 | 7.73 |
| 290 | 0.90 | 6.45 | 316 | 1.40 | 8.30 |
| 289 | 0.80 | 6.95 | 315 | 1.25 | 8.80 |
| 288 | 0.75 | 7.50 | 314 | 1.13 | 9.30 |
| 287 | 0.65 | 7.90 | 313 | 1.03 | 9.75 |
| 286 | 0.60 | 8.35 | 312 | 0.93 | 10.20 |
| 285 | 0.55 | 8.77 | 311 | 0.85 | 10.65 |
| 284 | 0.50 | 9.25 | 310 | 0.80 | 11.15 |
| 283 | 0.45 | 9.70 | 309 | 0.70 | 11.55 |
| | | | 308 | | 12.00 |
| | | | 306 | | 12.75 |
| | | | 304 | | 13.50 |
| | | | 302 | | 14.30 |
| | | | 300 | | 15.00 |
| | | | 298 | | 15.90 |

\* Critical Point
\*\* Value in parenthesis represents most pessimistic estimates of uncertainty -- see text.

the critical pressures based on curvature of the projections are on the order of only ±0.3 bar (Table 4). Significant curvature is shown only for the 380°C isotherm, corresponding to $\beta$ greater than $\frac{1}{2}$. Fluctuation theory predicts $\beta$ to be 0.32 (PITZER et al., 1987), but there is no theoretical explanation at present for $\beta$ greater than $\frac{1}{2}$. Critical compositions were estimated from the law of rectilinear diameters (ROWLINSON and SWINTON, 1982) by which the average mole-fraction NaCl of coexisting vapor and liquid pairs is plotted versus pressure and projected to the critical pressure of that isotherm calculated above. Uncertainty in critical composition is considerably larger than for critical pressure. The stated error for critical composition shown in Table 4 includes the composition range bracketed by the uncertainty in critical pressure, but has additional uncertainty which is difficult to quantify. The estimate of critical pressure is not greatly affected by slight variations in how the phase boundary is positioned through the experimental error bars. In contrast, the estimate of the critical composition is greatly affected by very slight shifts. The stated limits of uncertainty, therefore, include the maximum possible range resulting from using two extremes for the position of each phase boundary, and is no doubt an exaggeration of the uncertainty. Smoothed phase-boundaries were then constructed for each isotherm such that they passed through the critical point and the error bars of the experimental points. Table 4 summarizes values from these curves.

The critical points of the present study together with those from the literature are shown in Figs. 3 and 4. There is con-
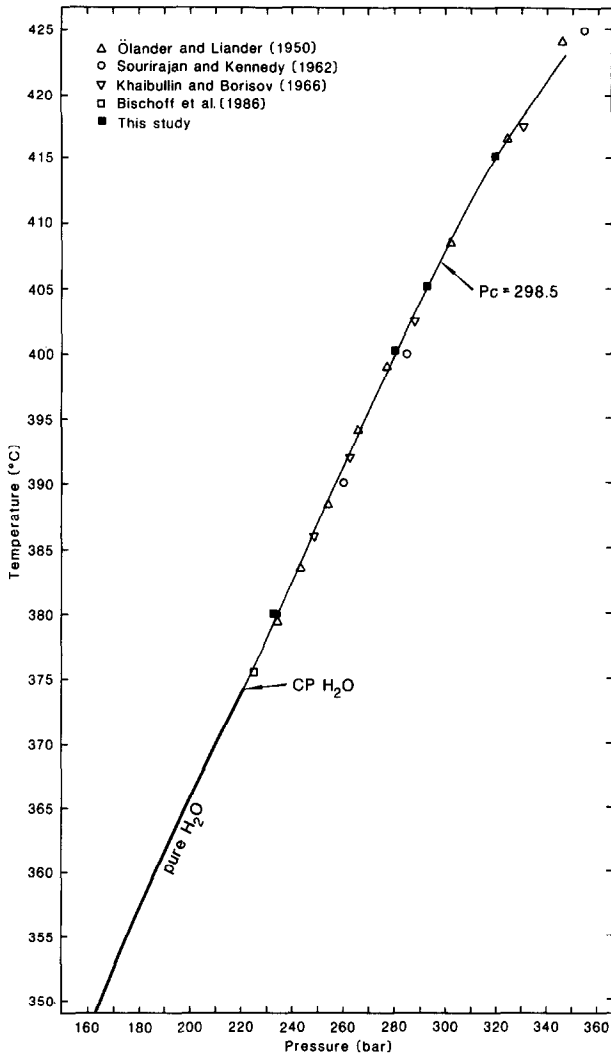
FIG. 3. *P-T* projection of compilation of experimentally determined critical points in the system NaCl-H₂O to 425°C. Symbol size of points from present study represents analytical uncertainty.

siderable agreement in the *P-T* projection (Fig. 3) illustrating the point that estimation of critical pressures is relatively accurate. The critical line of NaCl-H₂O is almost colinear with the saturation-pressure curve of pure steam. In contrast, the *T-x* projection of the critical line (Fig. 4) shows considerable disagreement among published values. Except for MARSHALL and JONES (1974) who estimated a temperature uncertainty of ±0.5°C, uncertainties were not stated in the studies cited above, so error bars could not be shown. Data from the present study are shown with two levels of error in wt% NaCl.

Table 5. Critical line for H₂O-NaCl from 375° to 415°C.

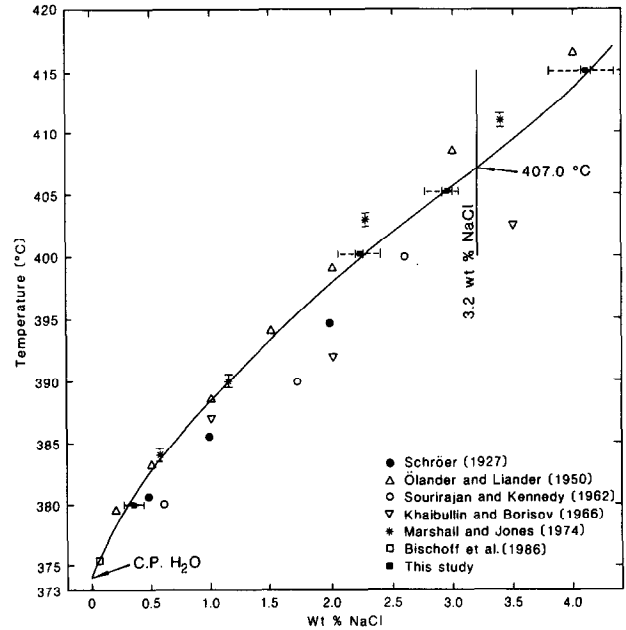| T° (C) | P (bars) | %NaCl |
|--------|----------|-------|
| 374.14 | 220.9 | pure H₂O |
| 375.0 | 223.0 | 0.035 |
| 380.0 | 234.0 | 0.32 |
| 385.0 | 245.4 | 0.68 |
| 390.0 | 257.3 | 1.15 |
| 395.0 | 268.9 | 1.66 |
| 400.0 | 280.5 | 2.24 |
| 405.0 | 293.5 | 2.93 |
| 407.0 | 298.5 | 3.20* |
| 410.0 | 306.0 | 3.56 |
| 415.0 | 320.5 | 4.13 |

* Seawater equivalent



FIG. 4. *T-x* projection of compilation of experimentally determined critical points in the system NaCl-H₂O from critical temperature of pure steam to 415°C. Nested error brackets for points from present study are explained in text. 407.0°C is the estimation of $T_c$ for seawater (3.2 wt% NaCl solution).

The narrower brackets result simply from the error range of critical pressure, while the wider brackets encompass the uncertainty associated with the extremes of position in the phase boundary alluded to above. A smooth curve was then drawn connecting the points from the present study and projecting to the critical point of water through the point at 375.5° previously determined (BISCHOFF *et al.*, 1986). This curve passes through points presented by MARSHALL and JONES (1974) and ÖLANDER and LIANDER (1950) from the critical point of pure water up to about 395°C, but deviates to higher NaCl contents at temperatures above. The effect of NaCl on the critical temperature is enormous, and curvature is marked. The explanation for this curvature is primarily a change in fluctuation effect as explained by PITZER (1986) and to a lesser extent, a variation in the degree of dissociation of NaCl along the critical line (LEVELT-SENGERS *et al.*, 1986). The curve crosses 3.2 wt% NaCl at 407.0°C, and this constitutes our estimate of the critical temperature of seawater. On Fig. 3, 407° corresponds to 298.5 bar which is our estimate of the critical pressure. Points taken at closely spaced intervals from Figs. 3 and 4 are tabulated in Table 5.

## REFERENCES

BISCHOFF J. L. and ROSENBAUER R. J. (1984) The critical point and two phase boundary of seawater, 200–500°C. *Earth Planet. Sci. Lett.* **68**, 172–180.

BISCHOFF J. L. and PITZER K. S. (1985) Phase relations and adiabats in boiling seafloor geothermal systems. *Earth Planet. Sci. Lett.* **75**, 327–338.

BISCHOFF J. L. and ROSENBAUER R. J. (1985) An empirical equation of state for hydrothermal seawater (3.2 percent NaCl). *Amer. J. Sci.* **285**, 725–763.

BISCHOFF J. L., ROSENBAUER R. J. and PITZER K. S. (1986) The system NaCl-H2O: Relations of vapor-liquid near the critical temperature of water and of the vapor-liquid-halite from 300 to 500°C. *Geochim. Cosmocim. Acta* **50**, 1437–1444.

HAAR L., GALLAGHER J. S. and KELL G. S. (1984) *NBS/NRC Steam Tables*, Hemisphere Publ., Washington, 320p.

KHAIBULLIN K. H., and BORISOV N. M. (1966) Experimental investigation of the thermal properties of aqueous and vapor solutions of sodium and potassium chlorides at phase equilibrium. *Teplofizika Vysokikh Temperatur* **4**, 518–523 (English translation, 489–494).

LEVELT-SENGERS J. M. H., EVERHART C. M., MORRISON G., and PITZER K. S. (1986) Thermodynamic anomalies in near-critical aqueous NaCl solutions. *Chem. Eng. Commun.* **47**, 315–328.

MARSHALL W. L. and JONES E. V. (1974) Liquid-vapor critical temperatures of aqueous electrolyte solutions. *J. Inorg. Nucl. Chem.* **36**, 2313–2318.

ÖLANDER A. and LIANDER H. (1950) The phase diagram of sodium chloride and steam above the critical point. *Acta Chem. Scandin.* **4**, 1437–1445.

PITZER K. S. (1986) Large-scale fluctuations and the critical behavior of dilute NaCl in H2O. *J. Phys. Chem.* **90**, 1502–1504.

PITZER K. S., BISCHOFF, J. L. and ROSENBAUER R. J. (1987) Critical behavior of dilute NaCl in H2O. *Chem. Phys. Lett.* **134**, 60–63.

ROSENBAUER R. J. and BISCHOFF J. L. (1987) Pressure-composition relations for coexisting gases and liquids and critical points in the system NaCl-H2O at 450, 475, and 500°C. *Geochim. Cosmochim. Acta* **51**, 2349–2354.

ROWLINSON J. S. and SWINTON F. L. (1982) In *Liquids and Liquid Mixtures*, chap. 3, Butterworth, London, 328p.

SCHRÖER, E. (1927) Untersuchungen über den kritischen Zustand. *Z. Phys. Chem.* **129**, 79–110.

SOURIRAJAN S. and KENNEDY G. C. (1962) The system NaCl-H2O at elevated temperatures and pressures. *Amer. J. Sci.* **260**, 115–242.