

## The Effect of Salinity on the Maximum Thermal Gradient of a Hydrothermal System at Hydrostatic Pressure<sup>1</sup>

JOHN L. HAAS, JR.

GL03528

### Abstract

The effect of salinity on the temperature-depth relations of a brine of constant composition, enclosed in a vein system, but freely connected to the surface, and everywhere at the boiling point for the hydrostatic head, was calculated by using a mathematical model. The Na-Ca-K-Cl brines which are found in thermal springs and in fluid inclusions in ore minerals were approximated by the available data for vapor-saturated NaCl-H<sub>2</sub>O solutions. In general, the results are similar to those calculated by D. E. White in 1968 for H<sub>2</sub>O, except that the gradients are steeper because of the increase in density and the decrease in vapor pressure caused by the dissolved salt. As a practical rule, the depth to an isotherm in a 5, 10, 15, 20, and 25 wt percent NaCl brine system is, respectively, 92, 84, 77, 70, and 63 percent ( $\pm 2$  percent) of the depth to the same isotherm in an H<sub>2</sub>O system. From the data presented, the minimum depth to the growth site of crystals containing fluid inclusions which indicate boiling of the brine can be estimated. Among other applications, these results are useful toward the understanding of the behavior of brines in geothermal areas which may or may not contain compositional stratification.

### Introduction

CONSIDER a geologic environment where a high heat flux is supported by means of mass movement of thermal water. White (1968) and White and others (1968) have observed at Steamboat Springs, Washoe County, Nevada, and at Yellowstone National Park, Wyoming, that the temperature of a brine at a given depth is often close to the boiling temperature for the corresponding hydrostatic pressure. The maximum thermal gradient in a mechanically open system is the gradient of a column of liquid of uniform composition which is at the boiling temperature for the corresponding hydrostatic pressure. If minerals were deposited in such an environment, they probably contain fluid inclusions which indicate the coexistence of volatile-rich gas phase and a salt-rich aqueous phase. When examining fluid inclusions in minerals from ore deposits, Roedder (1963, 1967, 1970), Kelley and Turneaure (1970), and Nash (1970) noted evidence for boiling of the mineralizing brines. Although boiling could be caused by effervescence of volatiles, in at least one occurrence the volatile content of the brine was small.

In the studies cited, and in others not discussed here, it would be useful to have available the depth-temperature relations for a column of liquid of given composition which is everywhere at the boiling point for the hydrostatic head developed by the overlying solution. In this paper, such profiles are supplied. The calculations were possible because the tempera-

ture of the fluid is known from the restriction that the vapor pressure is equal to the hydrostatic pressure. The data for vapor-saturated NaCl-H<sub>2</sub>O liquids were used as an approximation for the Na-Ca-K-Cl brines which are found in thermal areas and in fluid inclusions.

In making the calculations and in all subsequent discussions it was assumed that the liquid is open to the surface and contains no *suspended* vapor bubbles. "Open" specifies that the channels are continuous and without restrictions or throttling points such as would be generated by deposition of minerals in the channels. Such constrictions impede the flow and induce abnormal gradients in pressure and temperature, leading to pressures in the channel which approach lithostatic pressure and to temperature gradients above those predicted by the assumption that the hydrostatic pressure equals the vapor pressure.

A gas phase coexisting with the liquid in the channel is consistent with all arguments presented here provided the gas is contained in pockets and not *suspended* in the liquid of the channel. The gas trapped in pockets on the irregular walls of the channel is passive and does not alter the density of the column, but *suspended* gas bubbles decrease the average density of the column. Where *suspended* bubbles are present, the volume of gas is needed before depth-temperature relations can be predicted. The depth is proportional to the reciprocal of the density; therefore, use of the all-liquid data presented here would lead to the observation of steeper temperature gradients than would be predicted.

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

In a co  
change in  
and  $P$  is  
sion for  
a dimensi  
the units

In the si  
liquid is  
is 1.013  
hydrostat  
table.

Equati  
umn of  
In this  
and pres  
and solu  
was of  
The res  
trations  
solutions  
Cl brine  
sions an  
The effe

The  
 $dT/dT$   
to obtai

The lin  
respect  
Alge  
pressur  
functio  
fitting  
data.  
being  
resulti

The  
up to  
lower.  
C, can  
a prec

where  
the st  
perat  
aqued  
centr

## Source Data and Calculations

In a column of fluid of constant composition, the change in depth,  $\Delta h$ , between the pressure limits  $P_0$  and  $P$  is given by equation 1 where  $\rho$  is an expression for the density in terms of pressure,  $p$ , and  $c$  is a dimensional constant relating the unit of depth to the units of pressure and density.

$$\Delta h = h - h_0 = c \int_{P_0}^P \frac{1}{\rho} dp. \quad (1)$$

In the simplest case, where the top of the column of liquid is at sea level and open to the atmosphere,  $P_0$  is 1.013 bars (1 atm),  $h_0$  is 0 meters, and  $P$  is the hydrostatic pressure at some depth  $h$  below the water-table.

Equation 1 was integrated graphically for a column of  $H_2O$  by White (1968) using available data. In this exercise, the parametric relation of density and pressure to absolute temperature,  $T$ , was used, and solution of the general case, where the brine was of uniform composition,  $x$  molal, was obtained. The results of the integration for specific concentrations are supplied using the data for NaCl- $H_2O$  solutions to approximate the properties of Na-Ca-K-Cl brines which are commonly found in fluid inclusions and in the active Salton Sea geothermal system. The effect of  $Ca^{2+}$  and  $K^+$  are discussed.

The integrand of equation 1 was multiplied by  $dT/dT$ , that is, by 1, and the results were rearranged to obtain equation 2.

$$\Delta h = h - h_0 = c \int_{T_0}^T \frac{1}{\rho} \frac{dp}{dT} dT. \quad (2)$$

The limits  $P_0$  and  $P$  were replaced by  $T_0$  and  $T$ , respectively.

Algebraic equations for the density and vapor pressure of vapor-saturated NaCl- $H_2O$  liquids as functions of absolute temperature were developed by fitting semi-theoretical expressions to the available data. Detailed discussion of the procedures used are being presented elsewhere (Haas, 1970a, b). The resulting expressions are given below.

The density of vapor-saturated NaCl- $H_2O$  liquids up to saturation in halite or 7.3 molal, whichever is lower, and within the temperature range, 75° to 325° C, can be calculated from equations 2 through 4 with a precision of 0.002 g/cm<sup>3</sup>.

$$\rho = \frac{1,000 + Mx}{1,000V_0 + \phi x} \quad (\text{g/cm}^3) \quad (3)$$

where  $M$  is the molecular weight of NaCl,  $V_0$  is the specific volume (cc/gm) of  $H_2O$  liquid at temperature,  $\phi$  is the apparent molal volume of NaCl in aqueous NaCl (cm<sup>3</sup>/mole NaCl), and  $x$  is the concentration of NaCl in molal units (mole/1,000 g

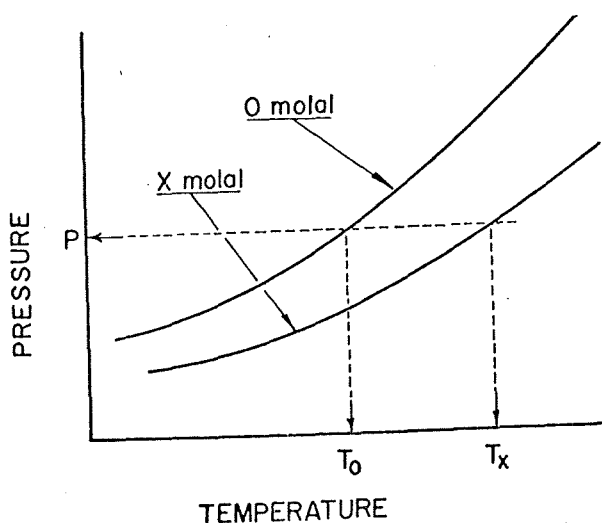


FIG. 1. Schematic representation of the relation between  $T_x$  and  $T_0$ .  $T_x$  is the temperature of a brine,  $x$  molal, and  $T_0$  is the temperature of  $H_2O$  liquid, 0 molal, at the same pressure  $P$ . The relation between  $T_x$  and  $T_0$  is given mathematically by equations 6 through 9. The vapor pressure of the brine is equal to the vapor pressure of  $H_2O$  liquid at  $T_0$  and is calculated from equation 10.

$H_2O$ ). The specific volume of  $H_2O$  liquid is calculated from equation 4 (modified from Smith and Keyes, 1934). The precision of equation 4 is 0.013 percent.

$$V_0 = \frac{V_c + a_1\theta^3 + a_2\theta + a_3\theta^4}{1 + a_4\theta^3 + a_5\theta} \quad (\text{cm}^3/\text{g } H_2O) \quad (4)$$

where  $T_x$  = temperature of the brine, kelvins.

$$\theta = 647.27 - T_x$$

$$V_c = 3.1975$$

$$a_1 = -0.3151548$$

$$a_2 = -1.203374 \times 10^{-3}$$

$$a_3 = 7.48908 \times 10^{-13}$$

$$a_4 = 0.1342489$$

$$a_5 = -3.946263 \times 10^{-3}$$

The apparent molal volume,  $\phi$ , is calculated from equation 5 (Haas, 1970a).

$$\phi = b_0 + b_1V_0 + b_2V_0^2 + x^3(b_3 + b_4V_0) \left( \frac{V_c}{V_c - V_0} \right)^2 \quad (\text{cm}^3/\text{mole NaCl}) \quad (5)$$

where  $V_0$  and  $V_c$  are the same as in equation 4 and the remaining constants are as follows:

$$b_0 = -167.219 \quad b_3 = -13.644$$

$$b_1 = 488.55 \quad b_4 = 13.97$$

$$b_2 = -261.07$$

TABLE 1a. Thermal Profile for H<sub>2</sub>O Liquid  
With Corresponding Vapor Pressure and Density

Temp. (°C)	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )
$T_b = 100.0^\circ\text{C}$	0.0	1.0	0.958
110	4.5	1.4	0.951
120	10.4	2.0	0.943
130	18.2	2.7	0.935
140	28.2	3.6	0.926
150	40.9	4.8	0.917
160	56.8	6.2	0.907
170	76.4	7.9	0.897
180	100.5	10.0	0.887
190	129.7	12.6	0.876
200	164.9	15.6	0.865
210	206.8	19.1	0.853
220	256.4	23.2	0.840
230	314.9	28.0	0.827
240	383.3	33.5	0.814
250	462.9	39.8	0.799
260	555.2	46.9	0.784
270	661.8	55.1	0.768
280	784.6	64.2	0.751
290	925.6	74.4	0.732
300	1088.	85.9	0.712
310	1273.	98.7	0.691
320	1487.	112.9	0.667
330	1732.	128.6	0.640
340	2017.	146.1	0.609
350	2350.	165.4	0.573
360	2746.	186.7	0.525
370	3243.	210.5	0.446

The vapor pressure of vapor-saturated NaCl-H<sub>2</sub>O solutions up to halite saturation and from 0 to 300° C can be calculated from equations 6 through 10 below, with a precision of 0.1 percent (Haas, 1970b); it can be extrapolated to 350° C without a loss in precision.

$$\ln T_0 = \frac{\ln T_x}{\alpha} \text{ (kelvin)}. \quad (6)$$

$T_x$  is the temperature of the brine and  $T_0$  is the temperature of pure H<sub>2</sub>O liquid at the same pressure as that of the brine. See Figure 1 for a graphical representation of the relation between  $T_x$  and  $T_0$ . The denominator,  $\alpha$ , is calculated from the following relations:

$$\alpha = d_0 + d_1 T_x \quad (7)$$

$$d_0 = 1.0 + d_{01}x + d_{02}x^2 + d_{03}x^3 \quad (8)$$

$$d_1 = 0.0 + d_{11}x + d_{12}x^2 + d_{13}x^3 + d_{14}x^4 + d_{15}x^5. \quad (9)$$

The values of the constants,  $d_{0i}$  and  $d_{1i}$ , are as follows:

$$\begin{aligned} d_{01} &= -4.76465 \times 10^{-5} & d_{11} &= 1.22999 \times 10^{-6} \\ d_{02} &= -2.11353 \times 10^{-5} & d_{12} &= 1.08716 \times 10^{-7} \\ d_{03} &= 8.03207 \times 10^{-6} & d_{13} &= -1.81761 \times 10^{-8} \\ & & d_{14} &= -8.39530 \times 10^{-10} \\ & & d_{15} &= 6.38341 \times 10^{-11} \end{aligned}$$

The vapor pressure of the brine at  $T_x$  is then calculated with equation 10 from the equilibrium vapor pressure of H<sub>2</sub>O liquid at the corresponding temperature,  $T_0$  (modified from Bain, 1964). The precision varies from 0.1 percent at 100° C to 0.4 percent at 350° C.

$$\ln p = e_0 + \frac{e_1}{z} + \frac{e_2 w}{z} (10^{e_3 w^2} - 1) + e_4 (10^{e_5 w^{1.25}}) \text{ (bars)} \quad (10)$$

where

$$\begin{aligned} w &= z^2 - e_6 & e_2 &= 3.1936 \times 10^{-4} \\ y &= 647.27 - T_0 & e_3 &= 1.1965 \times 10^{-11} \\ z &= T_0 + 0.01 & e_4 &= -1.0137 \times 10^{-2} \\ e_0 &= 12.50849 & e_5 &= -5.7148 \times 10^{-3} \\ e_1 &= -4.6169 \times 10^3 & e_6 &= 2.9370 \times 10^{+5} \end{aligned}$$

The differential of pressure with respect to temperature,  $dp/dT_x$ , was determined analytically from equations 6 through 10. The expressions for both  $p$  and  $dp/dT_x$  were then substituted into equation 2 and the integration was performed numerically by computer. A detailed statement of the mathematical treatment and a listing of the FORTRAN IV program are available from the author.

## Results

The thermal gradients for representative compositions in weight percent concentration units were calculated by the foregoing procedure and are given in Tables 1a and 1b and presented graphically on Figure 2. Also supplied on Table 1a and 1b are the vapor pressures (equivalent to the hydrostatic pressures) and the densities of the NaCl-H<sub>2</sub>O solutions. In calculating the results, temperature was treated as an independent variable. The uncertainty in the results for depth, pressure, and density are as follows:

- Depth  $\pm$  0.7 percent of the calculated depth.
- Pressure  $\pm$  0.2 percent at 100° C to  $\pm$  0.5 percent at 325° C.
- Density  $\pm$  0.002 g/cm<sup>3</sup>.

Temp. (°C)

$T_b$   
90.  
100.  
110.  
120.  
130.  
140.  
150.  
160.  
170.  
180.  
190.  
200.  
210.  
220.  
230.  
240.  
250.  
260.  
270.  
280.  
290.  
300.  
310.  
320.  
330.

 $T_b$ 

90.  
100.  
110.  
120.  
130.  
140.  
150.  
160.  
170.  
180.  
190.  
200.  
210.  
220.  
230.  
240.  
250.  
260.  
270.  
280.  
290.  
300.  
310.  
320.  
330.

TABLE 1b. Thermal Profiles for Selected Compositions of NaCl-H<sub>2</sub>O Liquids With Corresponding Vapor Pressures and Densities

The temperature at the water-table (P<sub>0</sub> = 1.013 b) is given at the bottom of each profile.

Temp. (°C)	2.0 Wt Per Cent NaCl			5.0 Wt Per Cent NaCl			10.0 Wt Per Cent NaCl		
	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )
T <sub>b</sub>	0.0	1.0	0.972	0.0	1.0	0.992	0.0	1.0	1.027
90.	-3.3	0.7	0.979	-3.4	0.7	1.000	-3.5	0.7	1.035
100.	-0.1	1.0	0.972	-0.3	1.0	0.993	-0.7	0.9	1.029
110.	4.2	1.4	0.965	3.9	1.4	0.986	3.2	1.3	1.022
120.	10.0	2.0	0.957	9.4	1.9	0.978	8.4	1.9	1.014
130.	17.6	2.7	0.949	16.7	2.6	0.970	15.2	2.5	1.007
140.	27.3	3.6	0.941	26.1	3.5	0.962	23.8	3.4	0.999
150.	39.7	4.7	0.932	37.9	4.6	0.953	34.8	4.4	0.990
160.	55.1	6.1	0.922	52.7	6.0	0.944	48.5	5.8	0.982
170.	74.3	7.8	0.913	71.0	7.7	0.935	65.6	7.4	0.973
180.	97.7	9.9	0.902	93.4	9.7	0.925	86.2	9.4	0.963
190.	126.0	12.4	0.892	120.5	12.2	0.915	111.3	11.7	0.954
200.	160.1	15.4	0.881	153.1	15.1	0.904	141.4	14.5	0.944
210.	200.8	18.9	0.869	191.9	18.5	0.893	177.2	17.8	0.934
220.	248.9	22.9	0.857	237.8	22.5	0.882	219.4	21.7	0.923
230.	305.5	27.7	0.845	291.7	27.1	0.870	269.0	26.1	0.912
240.	371.7	33.1	0.831	354.7	32.5	0.857	326.7	31.2	0.901
250.	448.6	39.3	0.817	427.8	38.6	0.844	393.6	37.1	0.889
260.	537.8	46.4	0.803	512.3	45.5	0.830	470.7	43.8	0.876
270.	640.5	54.4	0.787	609.6	53.3	0.816	559.3	51.3	0.863
280.	758.7	63.4	0.771	721.2	62.2	0.801	660.6	59.9	0.850
290.	894.3	73.6	0.753	849.0	72.1	0.784	776.0	69.4	0.835
300.	1049.5	84.9	0.734	994.9	83.2	0.767	907.3	80.0	0.820
310.	1227.2	97.5	0.714	1161.3	95.6	0.748	1056.2	91.9	0.804
320.	1430.7	111.5	0.691	1351.1	109.3	0.727	1225.0	105.1	0.787
330.	1664.3	127.1	0.666	1567.8	124.5	0.704	1416.3	119.1	0.768
	T <sub>b</sub> = 100.3°C			T <sub>b</sub> = 100.9°C			T <sub>b</sub> = 101.9°C		

Temp. (°C)	15.0 Wt Per Cent NaCl			20.0 Wt Per Cent NaCl			25.0 Wt Per Cent NaCl		
	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )	Depth (meters)	Pressure (bars)	Density (g/cm <sup>3</sup> )
T <sub>b</sub>	0.0	1.0	1.063	0.0	1.0	1.101	0.0	1.0	1.139
90.	-3.7	0.6	1.072	-3.9	0.6	1.110	-4.1	0.6	1.150
100.	-1.0	0.9	1.065	-1.4	0.9	1.104	-1.9	0.8	1.144
110.	2.6	1.3	1.059	1.9	1.2	1.097	1.1	1.1	1.137
120.	7.3	1.8	1.051	6.2	1.7	1.090	5.0	1.6	1.129
130.	13.6	2.4	1.044	11.9	2.3	1.082	10.2	2.1	1.122
140.	21.6	3.2	1.036	19.2	3.1	1.075	16.8	2.9	1.114
150.	31.7	4.3	1.028	28.5	4.0	1.067	25.2	3.8	1.106
160.	44.3	5.5	1.020	40.0	5.2	1.058	35.7	4.9	1.098
170.	59.9	7.1	1.011	54.3	6.7	1.050	48.6	6.3	1.089
180.	79.0	9.0	1.002	71.7	8.5	1.041	64.4	8.0	1.081
190.	102.0	11.2	0.993	92.7	10.6	1.033	83.5	10.0	1.072
200.	129.6	13.9	0.984	117.9	13.2	1.024	106.4	12.4	1.063
210.	162.4	17.0	0.974	147.8	16.2	1.015	133.6	15.2	1.055
220.	201.1	20.7	0.964	183.1	19.7	1.005	165.7	18.5	1.046
230.	246.4	25.0	0.954	224.3	23.7	0.996	203.1	22.3	1.037
240.	299.1	29.9	0.944	272.2	28.4	0.986	246.6	26.7	1.028
250.	360.1	35.5	0.933	327.6	33.7	0.977	296.8	31.8	1.019
260.	430.2	41.9	0.922	391.1	39.7	0.967	354.3	37.5	1.010
270.	510.5	49.1	0.910	463.8	46.6	0.957	420.0	44.0	1.002
280.	602.1	57.2	0.899	546.4	54.3	0.947	494.7	51.3	0.993
290.	706.1	66.3	0.887	639.9	62.9	0.937	579.0	59.5	0.985
300.	823.8	76.5	0.874	745.5	72.6	0.927	673.9	68.6	0.977
310.	956.8	87.8	0.861	864.2	83.3	0.916	780.4	78.7	0.969
320.	1106.7	100.3	0.847	997.3	95.2	0.906	899.3	90.0	0.962
330.	1275.3	114.2	0.832	1146.2	108.4	0.896	1031.7	102.4	0.954
	T <sub>b</sub> = 103.2°C			T <sub>b</sub> = 104.7°C			T <sub>b</sub> = 106.7°C		

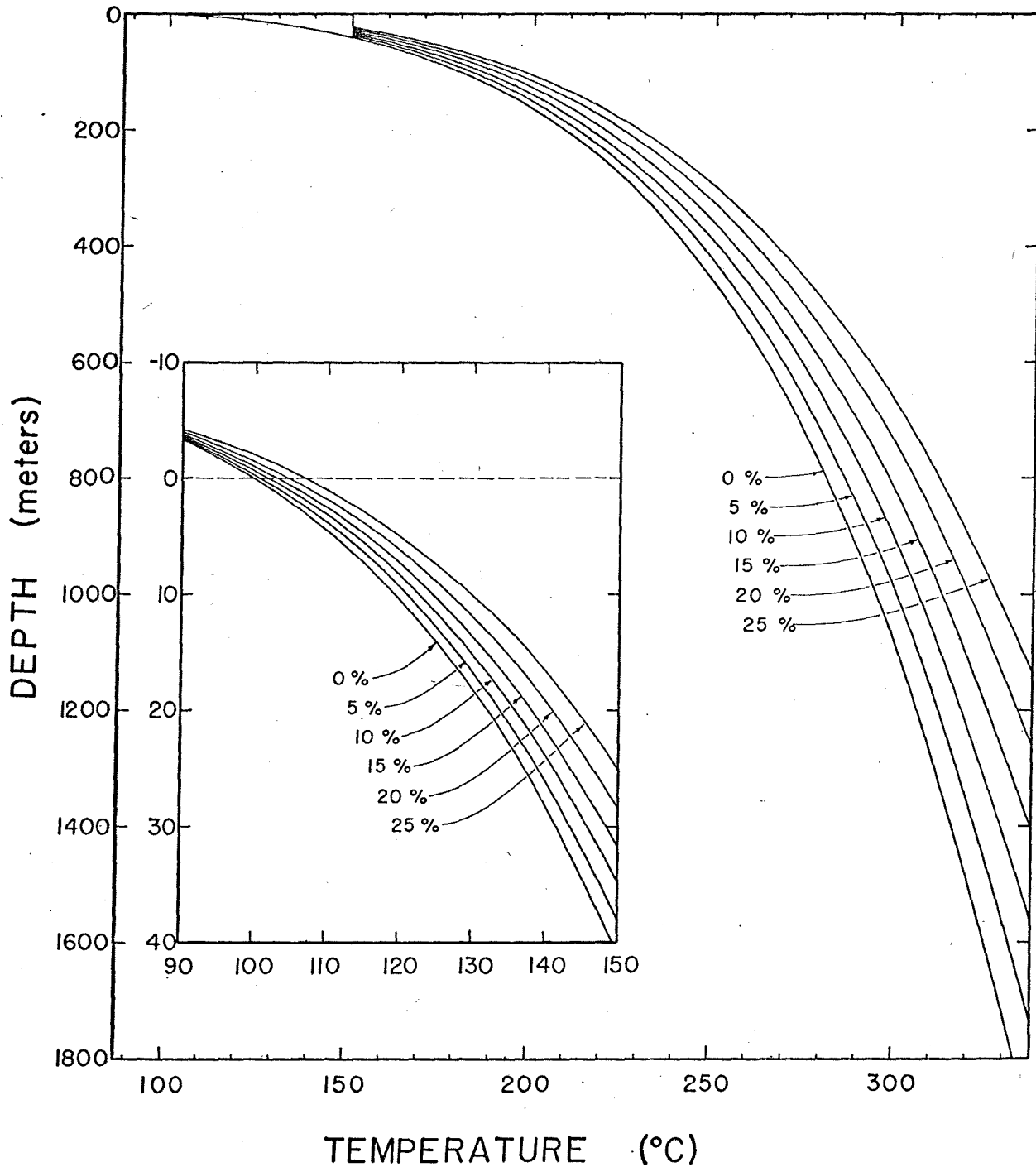


FIG. 2. Boiling-point curves for H<sub>2</sub>O liquid (0 wt percent) and for brine of constant composition given in wt percent NaCl. Insert expands the relations between 100° and 150°C. The temperature at 0 meters of each curve is the boiling point for the liquid at 1.013 bars (1.0 atm) load pressure which is equivalent to the atmospheric pressure at sea level. The uncertainty is contained within the width of the lines.

As indicated in the table, the depth to the 300° C isotherm, where the liquid is boiling H<sub>2</sub>O, is 1,087 meters, whereas the same isotherm is 674 meters below the water table if the liquid is uniformly 25 weight percent NaCl. Conversely, the temperature at 1 kilometer below the water table is 294° C for

boiling H<sub>2</sub>O and 328° C for boiling brine composed of 25 weight percent NaCl.

**Applications**

These results will be most useful to estimate the depth below the water table for the growth of a

cryst  
a bo  
dyna  
the  
temp  
pres  
that  
troll  
the  
the  
negl  
tiles  
is to  
ally  
also  
Any  
low  
will  
fecte  
posit  
If  
is ni  
is c  
fluid  
to a  
cont  
dicti  
zone  
be i  
rath  
C  
nary  
effe  
and  
mint  
give  
ing-  
der  
data  
a 1  
NaCl  
pres  
The  
the  
and  
mat  
and  
safe  
fero  
brin  
free  
T  
ful  
com  
exam  
mal

crystal which shows the evidence for development in a boiling liquid. The results are not applicable where dynamic two-phase equilibrium is established within the boiling column. For a discussion of such systems, refer to White and others (1971). Given the premise that a vein system is open to the surface, that the fluid pressure in the open system is controlled by the hydrostatic pressure developed by the column of liquid below the water table, and that the liquid is of constant molal composition, then neglecting the effect of dissolved or exsolved volatiles, the greatest depth at which boiling can occur is to be found where the liquid is everywhere virtually at the boiling point. This is so because this is also the condition of the lowest density in the column. Any other condition that lowers the temperature below the boiling point in part of the column of liquid will also increase the density of the liquid in the affected part and therefore decrease the depth to the position of the growing crystal.

If the composition of the liquid in the vein system is not constant, then making the assumption that it is constant (and equivalent to that found in the fluid inclusions of the mineral specimen) would lead to a prediction of too shallow a depth for a column containing a zone of more dilute brine and to a prediction of too great depth for a column containing a zone of more concentrated brine. The first error will be more likely, as near-surface water is generally rather dilute.

Concerning the effect of  $\text{CaCl}_2$  and  $\text{KCl}$ , preliminary information indicates that the error due to the effect of these solutes on density and vapor pressure and hence on the temperature-depth profiles can be minimized. In fluid inclusion work, the salinity, given as equivalent  $\text{NaCl}$ , is estimated from the freezing-point depression observed in a cooling stage under a microscope. Except for the uncertainty of the data, there is no difference in the boiling curves for a 1 molal  $\text{CaCl}_2$  or a 1 molal  $\text{KCl}$  solution and the  $\text{NaCl}$  solution which has the same freezing-point depression. This is amply demonstrated on Table 2. The estimation was made from the available data for the density of  $\text{CaCl}_2$  and  $\text{KCl}$  solutions (Rodnyanskii and others, 1962), a reliable technique for the estimation of vapor pressure of solutions (Stoughton and Lietzke, 1965, 1966; Lindsay and Liu, 1968), and the cited data for  $\text{NaCl}$  solutions. It is fairly safe to assume, therefore, that there is also no difference between the profiles of a typical  $\text{Na-Ca-K-Cl}$  brine and a  $\text{NaCl}$  solution which have the same freezing-point depression.

The results of these calculations could also be useful in discussing the behavior at the interface in a compositionally and thermally layered system; for example, at the interface between an upwelling thermal brine and meteoric water. Thermal brines at

TABLE 2  
EFFECT OF OTHER CHLORIDES

CONCENTRATION	FREEZING TEMP	DEPTH TO 300°C ISOTHERM	
		CALCULATED	PREDICTED (NaCl Data)
(molal)	(°C)	(meters)	
$\text{CaCl}_2$ : 1.00	-5.85	932 ( $\pm 2.5\%$ )	922 ( $\pm 0.7\%$ )
$\text{KCl}$ : 1.00	-3.25	981 ( $\pm 2.5\%$ )	989 ( $\pm 0.7\%$ )

or near the surface have been observed in the vicinity of the Salton Sea in southern California (White, 1955; White and others, 1963, Helgeson, 1968), near Gerlach, Nevada (White, 1955), and in deeps in the Red Sea (Degens and Ross, 1969). Boiling in the overlying dilute water can occur if the heat supplied by the thermal brine is sufficient to raise the vapor pressure of the dilute water above the hydrostatic pressure. Whether boiling will extend to the surface is controlled by the rate of diffusion of heat out of the boiling region into the cooler wall rock and to the surface, by the amount of heat expended in adiabatic expansion, but more strongly by the rate of convection of cooler denser near-surface water into the region of boiling, thus quenching the vapor phase that develops. If none of the above mechanisms are sufficient to quench the developing vapor phase, boiling will extend from the interface to the surface, and thermal springs will be observed.

Convection and mass transfer across the interface in the stratified system will not occur on a large scale because the density of the brine will be greater than that of the overlying ground water. One exception is the case where the vapor pressure of the brine exceeds the hydrostatic pressure. Mass transfer of liquid across the interface is then caused by the physical agitation produced by the rising gas bubbles.

A disparity in temperature at the concentration interface with its associated disparity in heat content will cause the overlying more dilute water to be heated and to boil by the acquisition of heat from the brine. The heat loss in the brine will cool the top of the underlying brine and cause a further increase in the density contrast. With a density contrast and the absence of boiling in the underlying brine, mass exchange across the interface will only be possible through chemical diffusion, a slow process. Because of the cooling which occurs in the lower layer and heating which occurs in the upper layer, convection cells will increase the rate at which heat is transferred from the heat source to the surface, which is the ultimate heat sink in the natural system.

Here, the temperature-depth relations were calculated for a liquid in an open vein system at constant composition. This is admittedly artificial and

is a limiting case. Salinity gradients should be expected. They can be caused by the boiling process which transfers water and volatiles upward, by reaction with the wall rock and by mixing with water of different composition. The maximum theoretical gradients of such an environment can be determined now if these changes in composition are describable in terms of the concentration of NaCl solution as some function of either temperature, pressure, or density. The approach in this situation is to substitute for the concentration term,  $x$ , in the foregoing equations, the algebraic expression which describes concentration as a function of temperature, pressure, or density and proceed with the necessary algebra. But, except for the mixing of solutions of two concentrations, the opportunity is small for recasting changes in composition into terms adequately described by the properties of a NaCl solution.

#### Summary

The temperature-depth relations were calculated for an open vein system where the liquid is everywhere virtually at the boiling point for the confining hydrostatic pressure. The pressure at the top of the open system is taken as 1.013 bars (1 atm), which is the pressure at sea level. The available data for NaCl-H<sub>2</sub>O solution were used as approximation for the Na-Ca-K-Cl brine which is found in natural systems and in fluid inclusions in ore minerals. The precision on the calculations using the NaCl-H<sub>2</sub>O model is 0.7 percent; this precision is better than the certainty that the NaCl-H<sub>2</sub>O model will be equivalent to the more complex brines. As a practical rule, the depth to an isotherm in a brine-filled vein system as a percentage of the depth to the same isotherm in a "pure-water"-filled vein system is as follows:

Wt percent NaCl:	0	5	10	15	20	25
Depth to isotherm as percent to the same isotherm in a salt-free system:	100	92	84	77	70	63
		(± 2 percent)				

From the data presented, it is possible to estimate the maximum depth below the water table at which a crystal grew if the inclusions in the crystal indicated there was boiling at the time of growth. Among other uses, the temperature-depth-composition-pressure-density data are also helpful to get an understanding of the physical processes which occur in such geothermal areas as Salton Sea or Yellowstone.

#### Acknowledgments

I wish to express sincere gratitude to my associates, D. E. White, E. W. Roedder, Al Truesdell, James R. Fisher, and particularly to P. B. Barton,

Jr., for the encouragement and the benefit of discussions on the topic of thermal brines. In no way are these associates responsible for the views and interpretations expressed here by me.

U. S. GEOLOGICAL SURVEY,  
WASHINGTON, D. C. 20242,  
January 25; March 22, 1971

#### REFERENCES

- Bain, R. W., 1964, Steam tables 1964: Edinburgh, Her Majesty's Stationery Office, 147 p.
- Degens, E. T., and Ross, D. A., ed., 1969, Hot Brines and Recent Heavy Metal Deposits in the Red Sea: Springer-Verlag, New York, 600 p.
- Haas, J. L., Jr., 1970a, An equation for the density of vapor-saturated NaCl-H<sub>2</sub>O solutions from 75° to 325°C: *Am. Jour. Sci.*, v. 269, p. 489-493.
- , 1970b, Thermodynamic correlations for brines: NaCl-H<sub>2</sub>O liquid-vapor equilibria: Written communication.
- Helgeson, H. C., 1968, Geologic and thermodynamic characteristics of the Salton Sea geothermal system: *Am. Jour. Sci.*, v. 266, p. 129-166.
- Lindsay, W. T., Jr., and Liu, C. T., 1968, Vapor pressure lowering of aqueous solutions at elevated temperatures: U. S. Office of Saline Waters, Devel. and Prog. Rept. 347, 235 p.
- Kelley, W. C., and Turneure, F. S., 1970, Mineralogy, paragenesis and geothermometry of the tin and tungsten deposits of the eastern Andes, Bolivia: *ECON. GEOL.*, v. 65, p. 609-680.
- Nash, J. Thomas, 1970, Personal communication.
- Rodnyanski, I. M., Korobkov, V. I., and Galinker, I. S., 1962, Ud'nenie obemi vodnikh rastvorov elektrolitov pri vysokikh temperaturakh: *Zhur. fiz. Khim.*, v. 36, p. 2216-2219.
- Roedder, Edwin, 1963, Studies of fluid inclusions II: Freezing data and their interpretation: *ECON. GEOL.*, v. 58, p. 167-211.
- , 1967, Fluid inclusions as samples of ore fluids: in Barnes, H. L., ed., *Geochemistry of Hydrothermal Ore Deposits*: Holt, Rinehart, and Winston, Inc., New York, p. 515-574.
- , 1970, Personal communication.
- Smith, L. B., and Keyes, F. G., 1934, The volumes of unit mass of liquid water and their correlation as a function of pressure and temperature. Part III. Steam research program: *Am. Acad. Arts and Sci. Proc.*, v. 69, p. 285-312.
- Stoughton, R. W., and Lietzke, M. H., 1965, Calculation of some thermodynamic properties of sea salt solutions at elevated temperatures from data on NaCl solutions: *Jour. Chem. Eng. Data*, v. 10, p. 254-260.
- , and —, 1966, Thermodynamic properties of sea salt solutions: U. S. Atomic Energy Comm., Oak Ridge Natl. Laboratory, Chem. Div. Ann. Prog. Rept. May 20, 1966, ONRL 3994, p. 84-86.
- White, D. E., 1955, Violent mud-volcano eruptions of Lake City hot springs, northeastern California: *Geol. Soc. Am. Bull.*, v. 66, p. 1109-1130.
- , 1968, Hydrology, activity, and heat flow of the Steamboat Springs thermal system, Washoe County, Nevada: U. S. Geol. Survey, Prof. Paper 458-C, 109 p.
- , Anderson, E. T., and Grubbs, D. K., 1963, Geothermal brine well: Mile-deep drill hole may tap ore-bearing magmatic waters and rocks undergoing metamorphism: *Science*, v. 139, p. 919-922.
- , Muffler, L. J. P., Truesdell, A. H., and Fournier, R. O., 1968, Preliminary results of research drillings in Yellowstone thermal area [abs]: *Am. Geophys. Union, Trans.*, v. 49, p. 358.
- , and —, 1971, Vapor-dominated hydrothermal systems compared with hot-water systems: *ECON. GEOL.*, in press.