A CALCULATION MODEL FOR THE P-V-T-X PROPERTIES OF GEOTHERMAL BRINES

R. W. Potter, III
U.S. Geological Survey
Menlo Park, CA.
and
J. L. Haas, Jr.
U.S. Geological Survey
Reston, VA.

A set of P-V-T-X data for the highly saline fluids encountered in some geothermal reservoirs is an important prerequisite to the modeling of the chemical and physical behavior of geothermal reservoirs. However, very limited data at the temperatures and pressures encountered in the geothermal systems are available (Potter, 1976). In this paper, we present relatively simple workable models which can be used to predict accurately both the density and vapor pressure of complex brines at elevated temperatures. Together these models yield a parametric equation of state for the vapor-saturated geothermal brine.

There have been attempts to erect theoretical models for calculating the density of complex brines, particularly seawater (Millero, 1973) but generally these models all represent some form of Young's Rule:

$$\phi_{vs} = \Sigma f_i \phi_{vi} \tag{1}$$

where ϕ_{vs} is the apparent molal volume of the solution, f_i is the mole fraction of component $\underline{i}$, and ϕ_{vi} is the apparent molal volume of component $\underline{i}$ for the total ionic strength of the solution. These models are generally inapplicable to the geothermal case because:

1. The modified Young's Rule defines components as ionic species and sums all the possible combinations of anions and cations. Presently, it is essentially impossible to accurately define the speciation in a highly saline fluid at elevated temperatures.

2. In order to apply the Rule, highly precise ϕ_{vi} data are required for all the species. At the present time densities of the required accuracy are available generally only at temperatures less than 50°C.

3. The modified Young's Rule as used by Millero (1973) assumes the additivity of the infinite-dilution volume properties. Although this holds fairly well for chlorides, it has not been generally documented for carbonates and sulfates. It is also questionable whether predictions based on such assumptions would work for highly saline fluids such as are encountered in the Salton Sea fields.

Since Young's Rule does however define the ϕ_{vs}, it follows by analogy that:

$$d_s = d_o + (d_1 - d_o)f_1 + (d_2 - d_o)f_2 \ldots (d_n - d_o)f_n \tag{2}$$

where d_s is the density of the solution; d_o is the density of H_2O; d_1, d_2, d_n are the densities of the binary salt-water systems of the same molality as the solution; and f_1, f_2, f_n are equal to the concentration (molality) of the respective salt divided by the molality of the solution. However, because water is simply one component of each binary solution it follows that:

$$d_s = d_1 + (d_2 - d_1)f_2 + (d_3 - d_1)f_3 \ldots (d_{n+1} - d_1)f_{n+1} \qquad (3)$$

where $d_1 < d_2 < d_3 \ldots < d_n$ for computational convenience. To test this relationship the density of NaCl (2.4034 molal)-KCl (1.1311 molal)-H_2O at 25°C was calculated using equations (2) and (3) as well as defining for equation (3) $d_1 > d_2 > d_3 > \ldots d_n$. All three methods yielded the same result, 1.1272 ± 0.0003 g/cm^3, which is in good agreement with the measured value of 1.1274 ± 0.0003 g/cm^3.

The only data of sufficient accuracy for complex solutions at elevated temperatures with which to test the density model are those for seawater (Fabuss et al., 1968). Data for the density of NaCl-H_2O, Kcl-H_2O, and $MgSO_4$-H_2O were taken from Fabuss et al. (1968), for $CaCl_2$ solutions from Potter and Clynne (1976), and for KBr-H_2O and $MgCl_2$-H_2O up to 100°C from the International Critical Tables (National Research Council, 1928). No data above 100°C were available for KBr and $MgCl_2$, hence they were calculated as KCl and $caCl_2$ respectively. At 100°C the calculated density was 0.9838 + 0.0005 g/cm^3 versus a measured density of 0.9839 ± 0.0005 while at 150°C the calculated density was 0.9443 ± 0.0015 g/cm^3 versus the measured density of 0.9451 ± 0.0010 g/cm^3.

White (1965) lists analyses for a Salton Sea brine sample whose density at 20°C is 1.264 ± 0.005. Based on the chemical analyses the brine can be approximated as a NaCl (2.592 molal)-Kcl (0.953 molal)-$CaCl_2$ (2.216 molal) brine. Using this composition and the data from Potter and Brown (1975, 1976) and Potter and Clynne (1976), the density of the brine was calculated as a function of temperature:

$$d_s = 1.2730 - 3.771 \times 10^{-4}t - 1.407 \times 10^{-6}t^2 \pm 0.002 \qquad (4)$$

Equation (4) yields a density at 20°C of 1.265 ± 0.002 g/cm^3 which is in excellent agreement with the measured density.

Predictive techniques for the vapor pressure of a solution are almost uniformly impractical for brines with a high content of dissolved solids. One technique, however, has proved fairly accurate for extrapolating data, observed at lower temperatures, to as much as 200°C to 300°C above the temperature range of the observations. A modified form of this technique, the reference substance principle (Othmer and Yu, 1968; Othmer and Chen, 1968), was used to derive a function for the vapor pressure of H_2O-NaCl solutions from the freezing temperature to 300°C with a precision of 0.32 percent of the observed vapor pressure (Haas, 1971a and b; 1975a and b).

The reference substance method can be derived from the Clapeyron equation for the vaporization of two liquids. Othmer and Yu (1968) have shown that the temperature T_x of a brine and the temperature T_o of the H_2O liquid (or reference substance) at the same pressure can be described by an equation of the following from:

$$\ln = T_o = m \ln T_x + c \qquad (5)$$

In the previous work on the H_2O-NaCl system (Haas, 1975a & b), it was found that one can improve the calculation by setting $c = 0$ and $m = (a + bT_x)^{-1}$. Equation 5 can be rewritten:

$$\ln T_o = (a + bT_x)^{-1} \ln T_x \qquad (6)$$

In previous work Haas has shown the model to be applicable to the simple binary system NaCl-H_2O. If one examines equation 6, it becomes obvious that as few as two well-defined observations could be used to predict the remainder of the P-T curve. To test this approach the data of Liu and Lindsay (1971) for a NaCl (1.7065 molal)-Na_2SO_4 (.1190 molal)-$MgCl_2$ (.2690 molal) brine were used at 75° and 100°C to define the constants <u>a</u> and <u>b</u> of equation 6. The calculated vapor pressure at 300°C agreed with the measured value to within 0.5 bars.

In preceding example, data at two temperatures which were 25° centigrade apart were used for the estimation of the vapor pressure. It is obvious that the greater the spread in the known data, the better the estimation, because errors in the known data have considerably less effect. Commonly available data for solutions are: 1) the freezing point depression (for dilute solutions), 2) the normal boiling point elevation where the vapor pressure of the brine is 1 atm or 3) osmotic coefficients near room temperature. From any two of these or from vapor pressures of the brine of interest, the constants <u>a</u> and <u>b</u> of equation 6 may be estimated.

The two models can be used to generate a PVTX grid for a geothermal brine. These data in turn can be used to generate a parametric equation of state from which the energy related thermodynamic properties, e.g. enthalpy, can be extracted.

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