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A THERMODYNAMIC MODEL FOR PREDICTING HCL PARTIAL PRESSURE ABOVE A HIGH TEMPERATURE HYPERSALINE GEOTHERMAL FLUID

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ABSTRACT

A thermodynamic model has been developed to predict the partial pressure of hydrochloric acid in equilibrium with high salinity fluids at temperatures up to 350°C. The model uses free energy of formation data obtained from heat of solution and electrochemical cell information. The model has been used to provide estimates for the concentration of HCl vapor in equilibrium with NaCl brines at temperatures, concentrations and compositions considered possible within the Geysers geothermal system. At 350°C, the maximum HCl content of superheated equilibrium steam is 8 ppmw at pH 5 and 3 molal NaCl. This concentration is an order of magnitude lower than HCl levels reported for northwest Geysers wells by Hazlip and Truesdell (1988), and suggests that an alternate mechanism may be needed to explain observed data.

INTRODUCTION

Recently several wells at the Geysers geothermal field have shown the presence of elevated levels of chloride ion in the condensate of produced steam(1). This chloride-rich condensate has been implicated as a possible major contributing factor to the high levels of corrosion observed in certain parts of the Geysers. More recently Haizlip and Truesdell (1) have suggested that the presence of chloride in produced steam is due to its generation from a high temperature chloride brine located deep in the formation. They have presented a model for predicting the concentration of HCl vapor in produced steam given a reservoir temperature, pH and salinity of the brine. Their model suggests that vapor-phase HCl concentrations of around 100 ppm could be produced by a reservoir brine containing 70,000 to 80,000 ppm chloride in contact with typical Geysers formation material at a temperature of 300°to 350°C.

Here we present a rigorous thermodynamic model for calculating the partial pressure of HCl in equilibrium with a sodium chloride brine. The model is simpler than that proposed by Hazlip and Truesdell and overcomes a number of theoretical and practical problems associated with their approach. Model predictions are in good agreement with experimental data on vapor pressures of hydrochloric acid solutions over a broad range of temperatures and acid strengths. When used to predict the HCl concentration of steam at reservoir conditions, the model gives values between one and two orders of magnitude lower than that given by Hazlip and Truesdell.

LIQUID-VAPOR EQUILIBRIUM MODELS

Previous models for the partitioning of hydrochloric acid between a liquid and vapor phase consider the following phase and chemical equilibria.

$$HCl(aq) = HCl(v) \qquad (1)$$

$$HCl(aq) = H^+(aq) + Cl^-(aq) \qquad (2)$$

Thus the vapor phase HCl is in equilibrium with a dissolved molecular species which, in turn, is in equilibrium with hydrogen and chloride ions. This type of approach to describe gas solubility has been success fully used before for volatile weak acid and bases in water. Examples of such systems are carbon dioxide, hydrogen sulfide and ammonia. Treating the solubility problem this way is most appropriate for systems in which the two equilibria can be experimentally decoupled. Such is the case in the aforementioned systems where the gases undergo only minimal dissociation in the aqueous phase. Then the equilibrium constants corresponding to reactions 1) and 2) can be unambiguously determined.

In the hydrochloric acid system the acid is almost completely dissociated and the two equilibrium constants cannot be independently measured. As a result, most experimental data such as electrochemical cell and calorimetric measurements are treated within a theoretical framework that disregards the possibility of an HCl ion pair and only allows for the presence of hydrogen and chloride ions. Then, all concentration dependence of thermodynamic properties for the system are contained in activity

coefficients of the ionic species which include the effect of dissociation as well as deviations from ideal solution behavior.

THE MODEL

The model we propose for predicting the vapor pressure of HCl is based on the following equilibrium (2)

$$H^+(aq) + Cl^-(aq) = HCl(v) \qquad (3)$$

By considering the above reaction between the ions in solution and gaseous hydrochloric acid we avoid having to construct a model which explicitly includes the formation of hydrochloric acid ion pairs. Another advantage of the above is that detailed and accurate thermodynamic data is available for all the species given in equation 3 at elevated temperatures and concentrations.

The equilibrium constant K associated with equation 3 is defined as:

$$K = \frac{f(HCl)}{a(H)a(Cl)} \qquad (4)$$

where f(HCL) is the fugacity of HCl vapor and the a's are activities of the ionic species in question. The equilibrium constant is given by;

$$K = e^{-\Delta G/RT} \qquad (5)$$

where

$$\Delta G = \mu(HCL(v)) - \mu(H^+) - \mu(Cl^-), \qquad (6)$$

R is the gas constant and T is the temperature in degrees Kelvin. The μ's are the molar Gibbs Free energies of formation for HCl in the ideal gas state at 1 atmosphere pressure or for respective ions in an ideal one molal solution. By convention, the free energy of formation of the elements and of hydrogen ion is equal to zero at all temperatures.

Free energy of formation data for HCl vapor was obtained from the Thermodynamics Research Center data base (3) and can be accurately represented by the following function of temperature:

$$G(HCL) = -21843 - 7.2896T + 0.72903T\ln(T) \qquad (7)$$

where T is in degrees Kelvin and G in calories/mole. For the chloride ion free energy of formation, data was obtained from Cobble, et al. (4) which was calculated using the high-temperature electromotive cell measurements of Greeley (5). This information was correlated using the following expression:

$$G(Cl^-) = -36823 + 40.167T - 6.9708T\ln(T) + 0.059788T^2 \qquad (8)$$

The resultant equilibrium constant was fit to the following function of temperature:

$$\ln(K) = 23.884 - 7539/T - 3.875111\ln(T) + 0.0300896T \qquad (9)$$

where, again, all temperatures are in degrees Kelvin and free energies of formation are in calories/mole.

Fugacity Coefficients

The equilibrium constant of equation 2 involves activities of ions in solution and the fugacity of gaseous hydrochloric acid. We wish to consider the solubility of the gas along the vapor-liquid line of water. For those combinations of temperature and pressure the fugacity of the gas can be approximated as equal to its partial pressure. Any corrections will be at most a few percent.

Activity and Osmotic Coefficients

For the activity coefficients of the ions we use the data of Holmes et. al. (6,7) and Pitzer (8) for HCl and NaCl solution for temperatures up to 300°C The data of Holmes is derived from a combination of their own flow calorimetry and electrochemical measurements with other enthalpy and electrochemical cell data. That information has been used to calibrate the Pitzer semiempirical electrolyte model and to test its predictive capabilities at elevated temperatures. The authors point out that the original Pitzer model produces excellent agreement with the data up to 250°C. At higher temperatures, the agreement becomes progressively worse and this, the authors state, is due to the increasing importance of ion pairing. It should be pointed out that the original Pitzer model did not ignore ion pairing but included it implicitly it its interaction coefficients. Subsequently, Holmes, et al. have extended the Pitzer model such that it can be applied to more concentrated solutions (16 molal) at higher temperatures (375°C) with, at most, a 10 percent error in the predicted versus observed results. This was done with a formalism that does not explicitly include ion pairing equilibria. Thus, for the concentrations of interest to us we feel that the Pitzer model and its extensions should provide an accurate method for calculating the thermodynamic properties of HCL-NaCl solutions at elevated temperatures.

MODEL EVALUATION

The model has been tested against experimental vapor pressure measurements over a broad range of temperatures and acid strengths (10,11). It produces excellent agreement with measured partial pressures of water and HCl from 25° to 110°C. For an evaluation of the model at temperatures more characteristic of geothermal systems we used the vapor pressure measurements of Staples (12) which extend up to 288°C and cover HCl concentrations ranging from 10 to 35 percent by weight HCl. For geothermal applications we will only consider for 10% HCl. Staples found that the total pressure, in units of psia, could be represented by the following equation

$$Ln(P) = 15.4744 - 4776.72/T \qquad (10)$$

where T is degress Kelvin. The average deviation between observed and calculated temperatures is 0.15% which corresponds to a deviation in the pressure on the order of 5 psi. A comparison was made between model and experimental data at temperatures of 250° and 275°C since this is in the temperature range of interest and should give an appreciable partial pressure of HCl. Since the data of Staples is for the total vapor pressure the partial pressure of water has to be determined. Its value is given by

$$P_{H2O} = a_w P^o_{H2O} \qquad (11)$$

where P^o is the vapor pressure of pure water at the temperature in question and a_w is the activity of the water in solution. The activity of the water is calculated from the osmotic coefficient using the following expression

$$a_w = e^{-2m\phi/55.51} \qquad (12)$$

where m is the hydrochloric acid molality and ϕ the osmotic coefficient. Table 1 lists mean activity and osmotic coefficients for both temperatures along with the appropriate equilibrium constants for reaction 1. In Table 2. we list the model -generated partial pressures of HCl and H2O and the total pressure, and the experimental values from Staples. The difference between the total pressures for model and experiment is approximately 0.7 and 0.85 percent at 250° and 275°C, respectively.

HCl Vapor Pressure at Reservoir Conditions

In order to estimate what the partial pressure of HCl will be at reservoir conditions we assume that the reservoir fluid can be characterized as a sodium chloride brine. Then the activity coefficient of the chloride ion and the osmotic coefficient of water can be predicted from the data of Pitzer and Holmes, et al. for NaCl solutions.

Using the above model we have calculated the vapor phase concentrations of HCl versus the liquid phase chloride concentration for pH values of 4, 5 and 6 at temperatures of 250°, 300° and 350°C. These are presented in FIGURES 1 through 3. With regards to the Geysers field this span of pH's should cover what can be reasonably expected from the mineral assemblages known to exist in the reservoir. The model results indicate that the HCl content of superheated steam in equilibrium with a NaCl brine with a geologically realistic pH is, for all practical purposes, zero below 300°C. At 350°C the model predicts that the maximum HCl content of superheated equilibrium steam is 8 ppmw at pH 5 and 3 molal NaCL. This is an order of magnitude lower than the HCl levels reported for northwest Geysers wells by the previous authors.

CONCLUSIONS

Results from the model we have presented suggest two general conclusions. If we accept the boiling brine hypothesis, then in order for the vapor to have an appreciable concentration of HCl, the reservoir pH must be considerably lower than the currently accepted value between 5 and 6 or the temperature is even greater than 350°C. Our model would indicate that the reservoir pH would need to be closer to 4 to produce 30 to 50 ppmw HCl in the steam phase at 350°C. Such a situation could only arise if the rock assemblage in contact with the brine is very different than what is currently believed to be present in the reservoir (1).

Conversely, if we accept a pH in the 5 to 6 range, then our model indicates that the HCl concentration in the steam would be negligible. Since chloride is observed in the steam at the Geysers, albeit at low concentrations, our model results call into question the boiling brine hypothesis. This possibility is supported by the unpublished experiments of Fournier (13) which show that appreciable amounts of HCl are only generated when the liquid phase of a chloride brine has essentially been boiled to dryness. This is further corroborated by the experiments of Pritchard, et al. (14) on the production of HCl vapor in boiler tubing from the injection of sodium chloride solutions into superheated steam. This might suggest that vapor phase HCl is

produced from superheated steam directly interacting with formation material or with a chloride-rich evaporite resulting from a localized dryout of the reservoir. In both of these situations it is imperative that the fracture network transporting the steam contain no mobile or immobile water, and that there is no exchange of liquid between fracture and bulk matrix rock. If this were not the case then any liquid present would tend to strip the HCl from the vapor until the concentrations were those predicted by the model presented in this paper.

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TABLE 1

Activity and osmotic coefficients and equilibrium constants for equation 3 for a 10% by weight HCl solution at 250° and 275°C.

T°C	γ	ϕ	K
250	0.34	0.858	2.6
275	0.23	0.779	8.9

TABLE 2

Measured versus calculated partial and total pressures, in units of psi, for a 10% by weight HCl solution at 250° and 275°C

	Temperature	
	250°C	275°C
P (H_2O)	524.4	791.1
P (HCL)	40.5	64.3
P total	564.9	855.4
P exp	568.9	862.8

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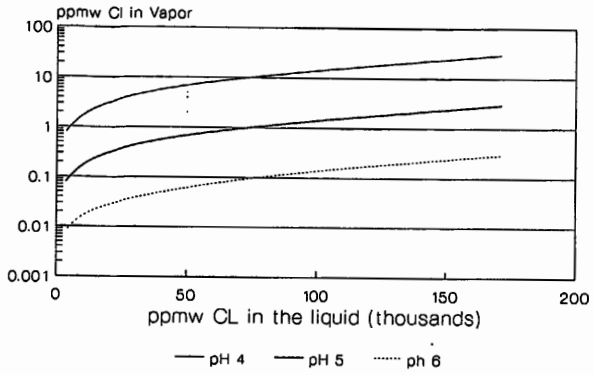
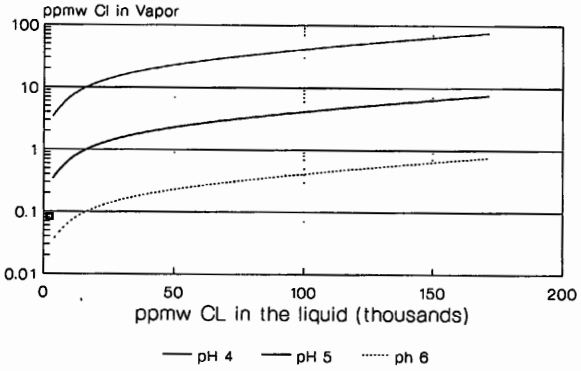
VAPOR VERSUS LIQUID PHASE CHLORIDE CONCENTRATION AS A FUNCTION OF pH



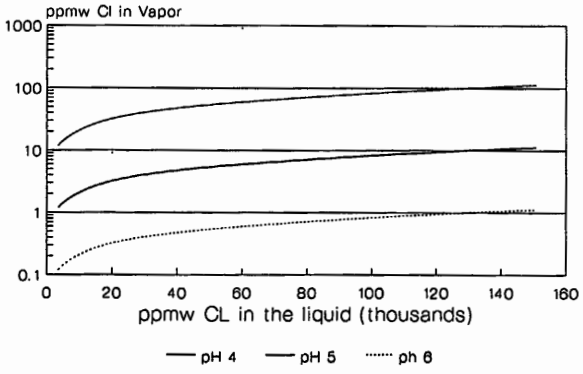
250 Deg C

VAPOR VERSUS LIQUID PHASE CHLORIDE CONCENTRATION AS A FUNCTION OF pH



300 Deg C

VAPOR VERSUS LIQUID PHASE CHLORIDE CONCENTRATION AS A FUNCTION OF pH



350 Deg C