PROCEEDINGS

"Geothermal Energy and the Utility Market - The Opportunities and Challenges for Expanding Geothermal Energy in a Competitive Supply Market"

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ABSTRACT

The UCSD brine chemistry program is providing highly accurate models of the behavior of high temperature brines to be used by the geothermal community to optimize production, interpret formation behavior and assist in performance assessment. (Models are now available as user-oriented programs packaged for both main frame and personal computers (IBM and Macintosh). A manual describing the models and their application to various geothermal problems has been developed and made available to potential users. Tutorial sessions have been held and future sessions are planned.

Present models can be used to predict the behavior of many important geothermal processes. For example, the tendency for production fluids to form carbonate, silica and sulphate scales can be predicted as a function of brine composition, temperature and CO₂ partial pressure. The breakout pressure (onset of two phase flow) can be calculated as a function of temperature and brine composition.) Preliminary models are available for characterizing H₂S gas/liquid distributions and the acid-base properties of the H₂S – H₂O system as a function of brine composition, temperature and pressure.

For the past year, a substantial part of our research has focused on the prediction of the properties of gasses in the CO₂ – CH₄ – H₂O system. We have developed highly accurate equations of state for each of the endmembers of the system for a pressure range of 0 to 8000 bar and temperatures from 0 to 1000°C. In order to treat the mixtures of importance to geothermal applications, a mixing model based on the endmembers has been developed. (The resulting equation of state for mixtures can be integrated analytically to obtain the free energies and enthalpies of the mixed gasses for a temperature range of 50 to 1000°C and pressures from 0 to 3000 bar.) Predictions of this model are within the accuracy of the experimental data and can predict the properties of the liquid phase, the gas phase and the coexistence of these phases with roughly equal accuracy.

(Most geothermal operations are significantly impacted by the chemical problems which result from the handling of geothermal fluids (production, energy removal and disposal). Control of these problems will determine how long these operations can be successfully carried out. Furthermore, it is necessary to minimize the costs of controlling chemical problems in order to make geothermal energy production economically competitive. Consequently, the Department of Energy (DOE) is supporting the UCSD in order to provide technology which will help reduce the risks associated with the chemistry of geothermal systems. The thermodynamic models we are developing for predicting the behavior of geothermal brine-solid-gas systems are highly accurate and flexible. In addition, these models summarize, generalize and extrapolate the available thermodynamic data for the brines and gas phases associated with geothermal power production. Thus, they provide an effective and low-cost tool for understanding the complicated chemistry of geothermal brines and for predicting and simulating this behavior. Design engineers and operations experts may reliably use this technology to optimize both the design and operation of geothermal power production systems.

At this time, models which treat a number of problems associated with the development and operation of geothermal power plants are available. They have been validated by extensive comparisons of their predictions with experimental data. The capabilities of the models we have developed to date are summarized in Table 1. Versions of the models have been developed for IBM, Macintosh and main frame computers (e.g., SUN). A manual outlining the development and operation of the models is available. Further model development is briefly reviewed in the following sections.

MODELS OF GAS THERMODYNAMICS

The scaling behavior and other important properties of geothermal fluids are very significantly affected by the presence of dissolved gasses. For example, the contribution of the partial pressures of insoluble gasses dissolved in the brine to the total pressure required to keep a geothermal brine in a single phase condition may exceed the contribution from the vapor pressure of the solvent. In such a situation, the insoluble gas composition will determine the conditions for the formation of two phases (breakout). In other situations (e.g., geopressed systems), an insoluble gas, such as methane, may be one of the energy products of the resource. Models which characterize the solubility of gasses in aqueous solutions and the thermodynamic behavior of gas mixtures are necessary to predict the behavior of such systems. Since transitions from gas to liquid behavior in near critical situations may be of interest, it is desirable to have these models extend continuously from liquid to gas regions.

Many important geothermal gas phase compositions fall within the CH₄ – CO₂ – H₂O system. In last year’s report, we discussed equations of state (EOS) that we had developed for
In the prior report, we discussed a set of mixing equations we developed which provides adequate representation of the data that we were able to obtain. However, while the agreement with the data is very satisfactory, there are several problems with these equations. The most important is that the mixing rules themselves are functions of pressure and therefore are not consistent with Eq.(1) when viewed as an expansion in the inverse volume. This means that Eq.(1) when applied to a mixture is not easily integrated to obtain other thermodynamic functions such as the free energy. Since the free energy is required to predict phase behavior, it is an essential property for geothermal applications. In order to provide a more useful representation of the data, we investigated an alternative form for the mixing equations which is loosely based on the virial expansion. In this form, the coefficients in Eq.(1) \( B, C, etc. \) are expressed as simple products according to the order of the density or inverse volume dependence of the appropriate term in Eq.(1). For example,

\[
B = \sum_{i<j} x_i x_j b_{ij} \quad (2a)
\]

\[
C = \sum_{i<j<k} x_i x_j x_k c_{ijk} \quad (2b)
\]

These equations and the method of evaluation of the parameters in Eq.(2) are explained in more detail in our recent publication (Duan et al., 1992b). The accuracy of the equations of state generated in this way is roughly equivalent to that of the earlier equation. However, this new equation of state may now be analytically integrated to give the free energy, enthalpy, etc.

We found that the above equations can describe both the PVT relations and the phase equilibrium properties of gas mixtures nearly within experimental accuracy. An example of the application of the new EOS to the prediction of liquid/vapor coexistence as a function of pressure and \( CO_2 \) composition for the important \( CO_2-H_2O \) system is given in Fig. 1. Note that the model is accurate for large ranges of temperature and pressure.

**FIRST PRINCIPLE PREDICTION OF PVT PROPERTIES**

The values of the parameters in Eq.(1) are determined from a large experimental data base. For many pressure and temperature ranges an adequate data base does not exist. This is particularly true for mixtures. For example, there are essentially no ternary data in the \( CH_4-CO_2-H_2O \) system. For this reason, we have initiated a program of direct simulation of PVT properties from first principles. Assuming the interactions between particles can be described by a simple Lennard-Jones potential, the motion for a representative system of particles may be calculated by integration of Newton’s equations of motion on a fast computer. By averaging over the simulated trajectories, the pressure and temperature may be calculated for a given energy and volume. We have carried out such a simulation with \( CH_4 \) as a representative gas system. Comparisons of simulated results with experimental values are given in Table 2. Remarkably, the result of these first principle simulations are within experimental accuracy for a very large range of temperatures and pressures. By fitting the results for extensive simulations of \( CH_4 \) and the available experimental data (Duan, Möller and Weare, 1992a), we have obtained an equation of the form of Eq.(1), which is a function of the volume and temperature. This equation now fits the simulated and measured data for a range of pressures from 0 to 20,000 bar and temperatures from 0 to 2000°C.

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**Table 1. PROJECT PROGRESS CAPABILITIES OF PRESENT MODELS**

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predict Behavior of Calcium Carbonate Scale Formation in NaCl and CaCl₂ Brines for ( T = 0^\circ ) to 250°C (PC Version Available)</td>
<td></td>
</tr>
<tr>
<td>Predict Solubility of ( CO_2 ) and ( CH_4 ) in NaCl Brines for ( T = 0^\circ ) to 250°C (PC Version Available)</td>
<td></td>
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<tr>
<td>Predict Solubility of Amorphous Silica Scale in Seawater-Type Brines for ( T = 0^\circ ) to 250°C</td>
<td></td>
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<tr>
<td>Predict Solubilities of Marine Scaling Minerals (NaCl, CaSO₄, etc.) to 250°C</td>
<td></td>
</tr>
<tr>
<td>Calculate Dissolution-Solution Characteristics of Rock-Water Systems Containing Na, K, Ca, Cl, and SO₄ for ( T = 0^\circ ) to 250°C</td>
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</tr>
<tr>
<td>Calculate Dissolution-Solution Characteristics of Rock-Water Systems Containing Na, K, Mg, Cl, and SO₄ for ( T = 0^\circ ) to 250°C</td>
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<tr>
<td>Predict Onset of Two Phase Behavior (Breakout) in NaCl Brines</td>
<td></td>
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<tr>
<td>Predict Solubility of Hydrogen Sulfide (( H_2O-H_2S-HS^- )) System (preliminary, ( 0^\circ ) - 90°C; 0 - 60 atm)</td>
<td></td>
</tr>
<tr>
<td>Predict Partial Fugacity in Mixed Gas System (( CO_2-CH_4-H_2O )) ( T = 0^\circ ) to 1000°C and ( P = 0 ) to 1000 bars</td>
<td></td>
</tr>
<tr>
<td>Predict Gas-Liquid Equilibrium in the ( CO_2-CH_4-H_2O ) system to 1000°C and 3000 bar</td>
<td></td>
</tr>
<tr>
<td>Predict Enthalpies of Brines (preliminary, ( 0^\circ ) - 250°C) and Gasses (preliminary, ( 0^\circ ) - 1000°C)</td>
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</tr>
</tbody>
</table>

the end members in this system. We showed that an equation can be developed that predicts PVT behavior within experimental accuracy for a range of pressure from 0 to 8000 bar and a range of temperature from 0 to 1000°C. This equation had the form:

\[
Z = 1 + \frac{BV}{V} + \frac{CV^2}{V^2} + \frac{DV^4}{V^4} + \frac{EV^5}{V^5} \quad (1)
\]

where \( B, C, D, E, F \) are functions of temperature. For a description of this equation, see our recent publication (Duan et al., 1992a). In order to obtain an equation of state for mixtures, it is common to extrapolate the single component behavior to mixed systems by assuming that the parameters in the EOS at constant temperature and pressure (e.g., \( B, C, D, etc. \)) are a function of the composition of the mixture. The equations (called mixing rules) chosen to describe the composition variation must return the parameter values for the end member systems. Beyond this condition, however, there is very little guidance as to the form that the mixing equations should take.
Because of the form of the potential chosen, the PVT simulations of a single gas can be generalized to another by simple scaling. The equation may be generalized to treat other systems as follows. We scale the temperature, pressure and volume as $P_8 = \frac{799.63}{T}$, $T_8 = 159.02 - \frac{1}{T}$ and $V_8 = \left(\frac{3.691}{\sigma}\right)^3 V$, where $\sigma$ and $\epsilon$ are Lennard-Jones parameters for the particular gas. Values of these parameters are available for many species. When L-J parameters are unavailable, they are easily evaluated using relatively few (≤ 20) PVT data. Now this equation will predict the PVT properties of many other systems, such as CO₂, N₂, CO, CH₄, O₂, H₂. Results of such calculations (see Table 3) indicate that for many systems extensive measurements may be replaced by simulations. Because of the paucity of data for many gas systems, this technology is important to meeting the DOE goal of being able to accurately predict the thermodynamics of geothermal gas-brine systems. We are expanding these simulations to include mixtures and a wider range of compositions. Results for the end member systems have been summarized and will be submitted for publication.

### ENTHALPY PREDICTIONS

This year we began a program to expand our calculations to include other thermodynamic properties of interest to the geothermal community with the general objective of producing a complete equation of state as a function of $T$, $P$ and composition for geothermal brines and the associated gas phases. One of the most important of these calculations is the enthalpy of the gas and liquid phases.

Since in the brine models we calculate the free energy as a function of temperature, the enthalpy may be calculated from the derivative,

$$\left\{ \frac{\partial (\Delta G/T)}{\partial T} \right\}_P = -\frac{\Delta H}{T^2} \quad (3)$$

Our modeling approach for describing the free energy as a function of temperature has been discussed in several publications (see, for example, Möller, 1988). Fig. 2 compares the enthalpy of aqueous NaCl solutions calculated by our model (Möller, 1988) with values determined by the extensive correlation of Pitzer et al. (1984). Note that the binary parameters for the NaCl system were evaluated by fitting both heat and free energy data (Möller, 1988; Pitzer et al., 1984). This is often the case for the binary parameters (Möller, 1988; Greenberg and Möller, 1989). However, many of the mixing parameters and all of the parameters for the slightly soluble salts were determined from free energy data alone. In these cases, when the free energy is differentiated in Eq.(3) there may be an increased error. We will be testing enthalpy calculations for other systems against available data in the near future.
In Fig. 3 we compare our model calculations of the enthalpy of the highly concentrated Salton Sea geothermal brine with that of pure water as a function of temperature. We note a difference of approximately 15%. This would create an error of similar magnitude in gas/liquid partitioning calculations which are an important geothermal application of enthalpy estimates. For example, in the constant enthalpy flash of a geothermal fluid from 300°C to 100°C, the error in the gas/liquid ratio would be about 20%.

The situation for gas phase models is somewhat different. In this case, we have an equation of state for the system as a function of volume. Integrating this equation gives the appropriate equation for the enthalpy as,

\[
\frac{\Delta H}{R T} = 2a_2 + 3a_3 T + \frac{2a_5 + 3a_4 T}{2V_f} + \frac{2a_8 + 3a_6 T}{4V_f^4} + \frac{2a_{11} + 3a_{12} T}{5V_f^5} + ...
\]

Using Eq. (1) for the pure water (solid line) system and for the H_2O-CO_2 (dashed line) mixed system, we obtain the results represented in Fig. 4 for the variation of enthalpy with pressure at T=200°C. Note that at this temperature the system undergoes vapor to liquid transition at P = 15.7 bar. Eq. (1) is essentially based on an ideal gas standard. Yet, as shown in Fig. 4, it gives fairly reliable results even for the latent heat. We note that for most geothermal systems the concentration of CO_2 in the liquid is very small. Fig. 4 shows that the enthalpy of the these solutions would be very nearly the same as that of the gas-free brine. In systems with low gas content, it may be more accurate to use the brine enthalpy as calculated in Eq. (3).

**APPLICATION: PREDICTION OF BOILING DEPTH OF GEOTHERMAL RESERVOIR**

As we saw in the above example, the presence of a small amount of CO_2 in a geothermal fluid does not significantly affect the enthalpy of the liquid state. However, the pressure at which the brine enters the two phase region at a particular tem-

![Fig. 3. A comparison of model calculations of the enthalpy of pure water (solid line) and of the enthalpy of a concentrated geothermal brine (dashed line, Salton Sea) as a function of temperature.](image)

![Fig. 4. A comparison of model calculations (using Eq. 1) of the variation with pressure of the enthalpy of pure water (solid line) and of the enthalpy of a H_2O-CO_2 mixture (dashed line). The solid squares are experimental data (Haar et al., 1984) for pure water enthalpies.](image)
perature is significantly affected. This of course determines the depth at which the brine boils in the formation. The following application of our models to scaling in the Steam Boat Geothermal Reservoir in Nevada illustrates this effect. The composition of the fluid is that of the W-235 Well (data supplied by Ted De Rocher, Yankee/Caithness). The fluids in this system contain an average of 3183 ppm CO₂. The temperature (solid line) and pressure profiles (dashed line) measured in the field are shown in Fig. 5. The breakout pressure calculated from our model is also plotted on the figure (dotted line). The fluid will boil when the vapor pressure of the fluid mixture is higher than the confining pressure. In this case, this occurs where the dashed and dotted lines intersect giving a boiling depth of approximately 2300 feet with a corresponding temperature and pressure of 192°C and 22 bar, respectively. This point is important since at breakout the CO₂ is preferentially removed from the fluid leading to significant supersaturation of the brine with respect to calcite. The composition of the vapor phase at breakout for a downhole temperature of 192°C is illustrated in Fig. 6 (point A). The composition of the vapor phase released (given by the solid line in the figure) is rich in CO₂ although there is a considerable amount of H₂O also in the vapor. As the pressure is lowered, the vapor becomes increasingly rich in H₂O and the fluid becomes more concentrated. This of course leads to a rapid supersaturation with respect to calcite and eventually to the precipitation of carbonate scale. We note in Fig. 5, however, that the predicted point of breakout does not coincide exactly with the appearance of scale (indicated by the asterisk) in the well bore.

In order to understand this discrepancy better we investigated how the supersaturation changes with depth in the well with the following model calculations. The SBGR brine was equilibrated with calcite at bottomhole formation conditions. Then, the resulting brine was gradually brought to surface conditions. Above 2300 ft, the calculated vapor pressure of the brine exceeded the pressure of the formation (see Fig. 5) and the system changed from one phase into two phases. The gas phase released has a relatively high concentration of CO₂ while the liquid phase is depleted in CO₂. The pressure is further reduced as the fluid moves up the well bore to surface conditions. The reduction in CO₂ and the loss of H₂O as steam leads to supersaturation with respect to calcite as shown in Fig. 7. Generally minerals will not precipitate until the fluid has reached significant supersaturation levels. However, at some point (usually SR ≈ 10) the calcite spontaneously precipitates as scale. The depth of scale formation observed in the well bore is shown by the cross in Fig. 7. At this depth, our model gives a corresponding SR value of about 12.5, which is entirely consistent with other experience involving calcite supersaturation. These results indicate that our model calculations can give a detailed description of the scale formation process in geothermal wells.
Fig. 7. The calcite saturation ratio predicted as a function of depth in Well 235-G, Steam Boat Geothermal Reservoir. The cross represents the depth at which calcite scale formation is observed.

REFERENCES


