Supercritical thermodynamics and fluid/fluid phase coexistence in thermodynamic systems: A corresponding states model and results of simulation

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Interpretation of thermodynamic processes in the lower crust, mantle and core are limited by the lack of data for the high temperatures and pressures characteristic of these regions. To contribute to the solution of this problem, we have developed corresponding states models and methods of simulation for closed electronic shell, non-polar systems. These methods can be used to extrapolate behaviour from lower temperatures and pressures to much higher T and P with accuracy close to that of experiments.

For sufficiently high temperatures, important components of natural fluids, such as CH_4, CO_2, H_2O, N_2, satisfy the non-polar and closed shell criteria. Their interparticle interactions can be well approximated by a potential of the form:

$$U_{ij} = \varepsilon\phi\left(\frac{r_{i,j}}{\sigma}\right) \qquad (1)$$

where ϕ is an arbitrary function and ε and σ are two temperature- and pressure-independent parameters. Under these conditions, the coresponding states theory shows that the thermodynamic functions of the system scale with the values of σ and ε. If an accurate free energy model is available for one species, with potentials well approximated by Eq. (1), all the thermodynamic properties of another species, also described by Eq. (1) but with different values of ε and σ, can be found by scaling the temperature and pressure. The value of σ and ε for a particular system can be calculated from limited data at low P and T or can be found in the literature.

We have developed a corresponding states model based on a highly accurate free energy equation for the CH_4 system. This equation of state was parameterized using the extensive experimental data available for this system as well as from simulation PVT data for high temperatures and pressures. Using this equation as a basis and values of σ and ε obtained from low P,T data sets, we have predicted PVT properties for species such as H_2O, CO_2 and N_2 that are better than those calculated by published models which were parameterized directly from data taken for these species.

To treat mixtures, the corresponding states model for pure systems may be generalized by assuming composition dependent σ and ε parameters calculated from the following mixing rules:

$$\varepsilon = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j k_{1,ij} \varepsilon_{i,j} \qquad (2)$$

$$\sigma = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j k_{2,ij} \sigma_{i,j} \qquad (3)$$

For sufficiently high pressures, fluid/fluid phase coexistence has been observed for the H_2O-N_2 system. Since the corresponding states model is based on a free energy description, phase equilibria and phase coexistence in the H_2O-N_2 system can be calculated using our free energy model of CH_4 and the mixing rules: Eqs. (2) and (3). Results are presented in Fig. 1. As in the case of PVTX data, the predicted compositions, temperatures and pressures are close to measured values. The only justification of the mixing rules given by Eqs. (2) and (3) is the

TABLE 1. compares predictions with data not used in the model parameterization

T(K)	P(bar)	X_{CO_2}	V_{EOS} (cm^3)	V_{exp}(cm^3)
1473.15	9500	0.787	38.20	37.51 ± .78
1573.15	14500	0.013	24.12	23.59 ± .35
1673.15	14500	0.237	25.50	25.91 ± .48
1673.15	19400	0.175	23.07	22.58 ± .22

Data of Frost and Wood (1997)

remarkable agreement they give with a very large amount of data in different systems.

In order to better understand the mixing behaviour in high temperature, high density fluids, we have developed a method of simulation based on the Gibbs ensemble method. Simulations of high density fluids are difficult because the particles are so restricted in their motion that equilibration is not easily reached. We have used Monte Carlo strategies to equilibrate the system and obtain average behaviour. Using the simple Lennard-Jones potentials, we obtained predictions that are close to our equation of state predictions and to experimental data. These results suggest that with attention to choice of phenomenology and careful parameterization, thermodynamic models can be developed that provide accurate predictions for the very wide ranges of temperature, pressure and composition required for treating earth processes.

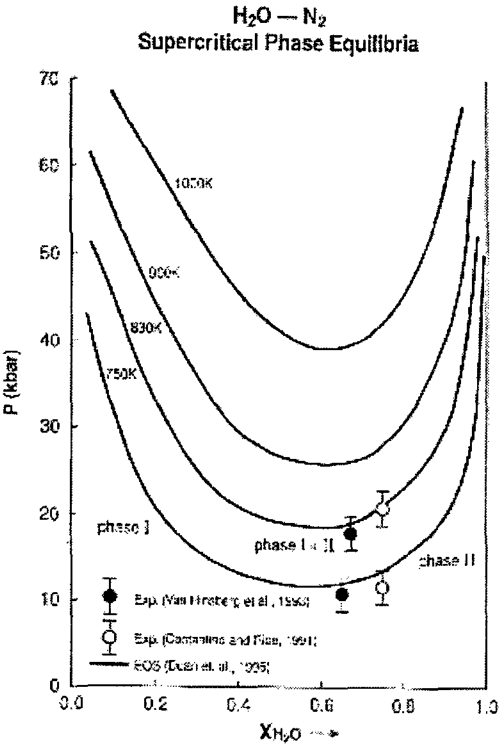

FIG. 1.