THEORETICAL MODELING OF GEOCHEMICAL FLUIDS UNDER HIGH-PRESSURE, HIGH-TEMPERATURE CONDITIONS

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Methods of statistical physics of fluids have proved to give reliable estimates of properties of geochemically important volatile components under thermodynamic conditions where experimental data are scarce and difficult to obtain.

RESUME: Les méthodes de physique statistique des fluides ont conduit à une bonne estimation des propriétés de composés volatiles géochimiquement importants dans des conditions thermodynamiques difficiles a mettre en oeuvre.

For a prediction of mineral-fluid equilibria and solubility of minerals at crustal and upper mantle conditions a quantitative thermodynamic description of the fluid (i.e., equation of state) is required. Empirical and semiempirical equations, fitted to available experimental data, are widely used nowadays in geochemical literature for such purposes. These equations, however, cannot be reliably extrapolated beyond the pressure-temperature range of available data. In such cases theoretical methods of statistical physics of fluids, though much more elaborate than empirical ones, can give a reasonable solution. Two approaches to the problem are shortly discussed below.

An asymptotically accurate (in the limit of high T-P) equation of state for the Lennard-Jones fluid developed by means of thermodynamic perturbation theory has been used to obtain densities and fugacities of CO₂, CH₄, CO, H₂, N₂ and Ar up to 100 kbar and 2000 K. All of these molecules possess a rather small, if any, anisotropy of intermolecular interaction, which may be taken into account using a so-called "effective" intermolecular LJ-potential. Temperature-dependent parameters of the potential were determined by the regression of available P-V-T data in the limited P-T range. Advantages of the proposed theoretical equation of state over empirical ones are clearly seen in Fig.1 which presents the comparison of CO₂ fugacities calculated from different equations widely used in geochemical literature (see Ref.3,4 and references therein) with experimental data on decarbonation of enstatite, forsterite, geikielite and wollastonite at high temperatures and pressures. A more detailed analysis of the equations also suggests that an extrapolation to higher temperatures and pressures via the theoretical equation seems to be more reliable, though any experimental data are still not available in this region.

This approach can be easily extended to mixtures of the above mentioned fluids using ordinary mixing rules for effective parameters of the Lennard-Jones intermolecular potential.

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Because of a strong anisotropy of intermolecular water-water interactions the above approach cannot be directly applied to aqueous fluids which are most interesting from the geochemical point of view. Monte Carlo and Molecular Dynamics methods of computer simulation, which have already proved to be powerful tools to study aqueous solutions at normal pressures and temperatures, seem very promising in this case.

Thermodynamics and structure of water along two supercritical isotherms of 673 and 773 K and in the pressure range from 0.3 to 30 kbar have been studied by the Monte Carlo method with a TIP4P intermolecular potential. Technical details of the simulation as well as the full analysis of thermodynamic and structural results obtained will be published elsewhere. The values of density, enthalpy, isobaric heat capacity, isothermal compressibility, and thermal expansion coefficients were obtained and found to be in good agreement with available experimental data. Some thermodynamic results are shown in Figs. 2 and 3.

Figure 1. Fugacity of CO\textsubscript{2} at high pressures and temperatures. Dashed, dot-dashed and dotted lines are calculated using equations derived by Holloway, Bottinga & Richet, and Saxena & Fei, respectively (see Ref. 3, 4 and references therein). Full lines are calculated using the theoretical equation of state\textsuperscript{6}. Squares and circles with error bars are CO\textsubscript{2} fugacity values estimated from experimental data on decarbonation reactions at high temperatures and pressures\textsuperscript{6}.

Figure 2. Densities (squares, right scale) and isobaric heat capacities (circles, left scale) of water at 773 K and high pressures, obtained from Monte Carlo simulations. Full lines represent equation of state for water\textsuperscript{8}, fitted to all existent experimental data within experimental errors.

Figure 3. Distributions of pair interaction energies in supercritical water at 773 K and pressures of 30, 10, 1, and 0.5 kbar (full lines, from the top to the bottom, respectively). The dot-dashed line represents the same distribution in normal liquid water. Units for the ordinate are mole per cent per kJ/mol.
At high pressures and temperatures water almost completely loses its specific features and behaves both thermodynamically and structurally like a simple argon-like liquid. However, the shape of the O-H radial distribution function clearly indicates\(^{10}\) that hydrogen bonding still persists under conditions studied.

Pair energy distributions, which represent the distribution of dimer energies, give an insight into molecular rearrangements taking place in water under such conditions. These functions for water at 773 K and in the pressure range from 30 to 0.5 kbar are shown in Fig. 3 as full lines. The same distribution for liquid water under normal conditions is shown for comparison as the dot-dashed line. Though the maximum at low energies has already disappeared, a distinct shoulder is clearly seen at the same range of energies, indicating that hydrogen bonding still persists to some extent under the conditions studied.

At 773 K and 10 kbar (the second curve from the top in Fig. 3) the density of supercritical water is virtually the same (\(\approx 1 \text{ g/cm}^3\)) as that of liquid water at 298 K and 1 bar (dot-dashed curve). Therefore average intermolecular distances are also virtually the same in the two states. The comparison of both curves gives the opportunity to observe the pure effect of a significant pressure and temperature increase along an isochore on the shape of the distribution. The width and the height of the main maximum (beyond the scale of Fig. 3) remain almost unchanged as well as the shape of the repulsive part of the distribution at positive energies. However, a certain amount of interacting molecular pairs are redistributed from the hydrogen-bonding range of energies (\(\approx -25 \div -15 \text{ kJ/mol}\)) to the non-bonding range (\(\approx -15 \div -6 \text{ kJ/mol}\)). This indicates, that significant changes are taking place in the near-neighbourhood of a molecule as the pressure and the temperature increases, despite the virtually unchanged density and average intermolecular distances.

Such an analysis will be even more informative in the case of complex hydrothermal solutions, where solute-solute, solute-solvent, and solvent-solvent distributions can be accumulated separately during the simulation. A Molecular Dynamics simulation of supercritical alkali-halide solutions is currently in progress.

It can be concluded, that although theoretical methods of statistical physics of fluids require much more computational efforts than empirical and semiempirical methods widely used in geochemical literature\(^2,^4\), they allow one to get more reliable data on the properties of natural fluid systems under extreme conditions, which are often unaccessible by other methods, including experimental ones. They also may serve as a valuable source of data necessary for an extension of presently used thermodynamic models\(^1,^2\) over wider ranges of pressure and temperature.