Thermodynamic Properties of Natural Fluids at High Temperatures and Pressures

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The accurate description of the thermodynamic properties of natural fluids at P-T conditions of typical geological processes remain to be a unsolved problem. Natural fluids are complex mixtures of various chemical components. Its composition can vary significant from almost pure water to highly saline brines. Many empirical equations of state (EOS) have been proposed for such fluids. But all of these EOS suffer from the same limitations - they can be used only for interpolations. To put this in the other words, such EOS can not be effectively applied outside the range where experimental measurements are available. The thermodynamic properties of the principals fluid components (H_2O, CO_2, CH_4, N_2) are well known experimentally. Properties of mixtures are much less investigated or available only in limited P-T ranges. Most experiments have been carried out for binaries, while the results for more complex systems are relatively rare. However, there are fluid components relevant to the geochemical processes which properties remain unknown at high pressures and temperatures even as pure fluids.

The most promising solution for this problem is to use a theoretical equation of state. Recently, we proposed an EOS for the mixtures of non electrolytes which is based on the thermodynamic perturbation theory. This EOS approximates the behaviour of the molecules in the fluids by the model of "Lennard-Jones" dipolar spheres. Only dispersion forces, dipole-dipole and dipole-induced dipole interaction between molecules were taken into account. To derive the parameters for the interaction potential available experimental P-V-T data were used. While the law of interaction between molecules is independent on P and T, the model fitted to the experimental data in one P-T range will be also accurate at other conditions. Therefore this EOS can be extrapolated and used for complex multicomponent fluid mixtures.

The main advantages of this approach, can be shortly summarised as follow: 1) The EOS includes only four component specific parameters with clear physical meaning (dipole moment, polarisability and two parameters of the Lennard-Jones potential). 2) The EOS can be safely extrapolated to higher temperatures and pressures besides the ranges of available P-V-T measurements. 3) The properties of fluid mixtures are determined from that of the pure fluid components. No additional parameters are involved. 4) New components can be easily added. The model can be used as a basis for more general fluid systems involving strong electrolytes.

Despite of the simplicity, the model considers two major classes of fluid compounds which are polar and non-polar gases. The EOS actually provides the thermodynamic properties of mixtures of 20 polar and 25 non-polar components in the system H-O-C-N-S-F-Cl-Br-I-B-Si-He-Ne-Ar-Kr-Xe. For many of them experimental data are not available at high temperatures and pressures. Therefore, we discuss a simple method used to derive parameters of the EOS from low temperature vapour-liquid equilibria data or critical properties of pure the fluids.

The available experimental studies of phase relations in the H_2O-N_2(-CH_4, -H_2) binaries, suggest that in the fluid mixtures of highly polar molecules with non-polar ones, high pressure phase separations occur at the temperature above the critical point of the polar component. The extend of the high pressure immiscibilities in the fluids of non-electrolytes based on the EOS and the influence of the fluid composition on the mineral equilibria at high temperature and pressures will be discussed.