

EOS for multi-component fluids

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For the understanding of processes in the crust and upper mantle thermodynamic properties of complex fluids including electrolytes are required. For pure neutral fluids with one or few components such *equations of state (EOS)* are available. For electrolytes at moderate physical conditions the choice is even more limited. Today in petrology for the calculations of complex solid-fluid phase diagrams, fluids are still treated as it would consist of distilled water. It is therefore necessary to have an *EOS*, which is capable of treating multi-component fluids in the complex systems. Such an *EOS* must species orientated and it would be desirable, that such an approach is in principal extendable to electrolytes.

On the basis of the *Helmholtz free energy A*, for neutral fluids *EOS* are available (e.g. [1]). By differentiation of *A* in respect of temperature *T* and/or density ρ , all thermodynamic properties can be derived. For the formulation of these *EOS*, *A* is split into an ideal gas and a residual term and have been proven to be precise and extrapolatable to *T* and ρ relevant for the upper mantle. The necessary parameters are not based on physical properties but are empirical and mixing parameters have to be fitted separately to experimental data [2].

Using perturbation theory and spherical harmonics expansions, the residual part of *A* can be formulated using electrical moments, polarizabilities, and deviations from spherical symmetry for repulsion (e.g. [3, 4, 5]). This approach is extendable to mixtures. Applying [3, 4, 5] fully, an *EOS* for *A* in the system H-He-C-N-O-Ne-Ar-Kr-Xe is presented. Instead of approximating the *Lennard-Jones* by a perturbation of hard-spheres, a direct approach is applied using an *EOS* for a *Lennard-Jones* fluid [6]. The necessary dipole-, quadrupole, octupole-moments, polarizabilities, and heat capacities are taken either from literature or calculated by *ab initio* methods. The remaining parameters for the *Lennard-Jones* fluid for each species ϵ_i , σ_i , and any non-spherical repulsion contributions are fitted by generated *A*-values as a function of *T* and ρ from the *EOS* of pure fluids (e.g. [1, 2]). For mixtures respective mixing rules are available. Because the *EOS* is based on species, H-bonds can be also included. Extension to electrolytes seems possible.

[1] Wagner & Pruß (2002) *J. Phys. Chem. Ref. Data* **31**, 387-535. [2] Kunz & Wagner (2012) *J. Chem. Eng. Data* **57**, 3032-3091. [3] Gubbins & Twu (1978) *Chem. Eng. Sci.* **33**, 863-878. [4] Moser *et al.* (1981) *Fluid Phase Equilibria* **7**, 153-179. [5] Shukla *et al.* (1983) *Fluid Phase Equilibria* **15**, 125-172. [6] Thol *et al.* (2016) *J. Phys. Chem. Ref. Data* **45**, 023101-1-36.