Thermodynamic description of geochemical important aqueous non electrolytes in the wide range of state parameters

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The virial equation approach for description the thermodynamic properties of aqueous non electrolytes is proposed. It is based on the precise equation of state for the solvent (H_2O) given by Hill (1990) and requires only three empirical parameters that are independent on temperature and pressure. The standard state chemical potential of the dissolved species at given pressure P and temperature T can be expressed as:

$$\mu^0_{aq}(P,T) = \mu^0_g(T) + \tilde{R}T(-\ln(55.51) + \ln f^0_1 + 2\rho^0_1 \cdot \Delta B_\rho$$

where $\mu^0_g(T)$ is the chemical potential of the associated pure gaseous component at standard pressure (1 bar), $\tilde{R}$ is the gaseous constant, f^0_1 and

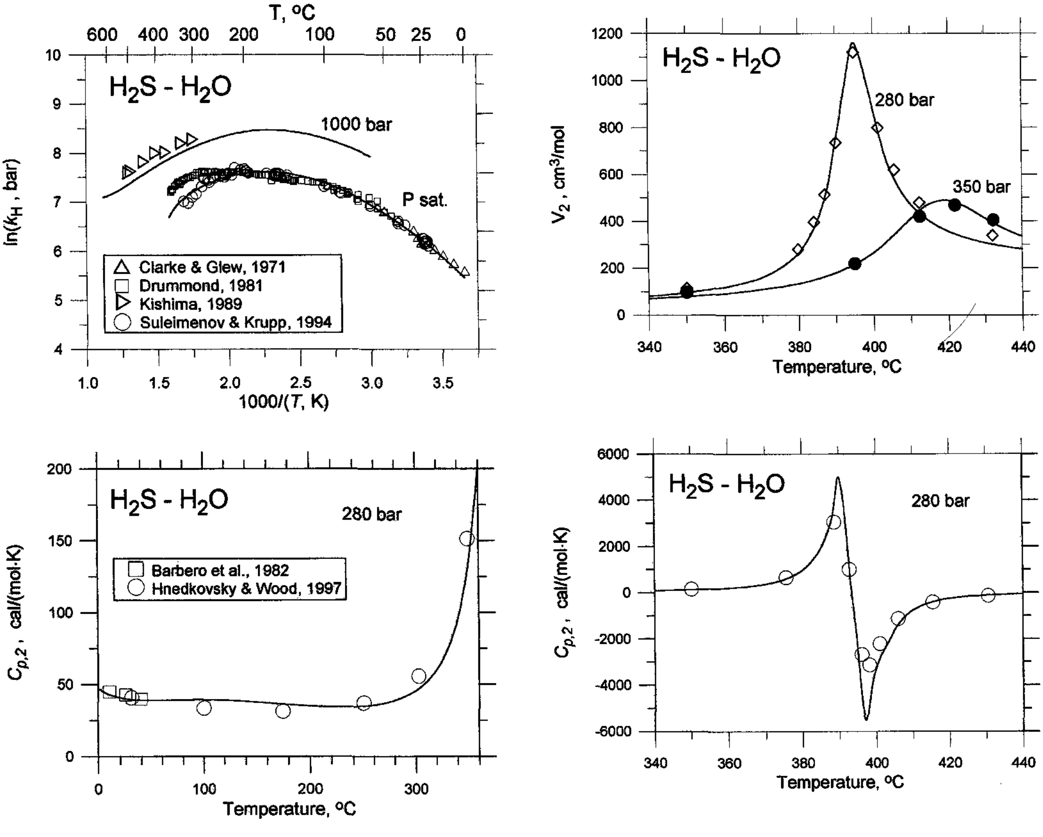

FIG. 1. Comparison between theoretical prediction (lines) and the experimental data (symbols) for various thermodynamic properties of aqueous H_2S. Symbols without nomenclature correpospond to the data from Hnedkovsky and Wood (1997).

ρ_1^0 are fugacity and density of pure solvent (H_2O), respectively, and $\Delta B_\rho \equiv B_{12} - B_1$ stands for the difference in the virial coefficients that characterizes interaction non electrolyte-H_2O and H_2O-H_2O, respectively. Differentiating the master equation with respect to pressure and temperature expressions for partial molar properties of the dissolved component could be derived:
volume

$$\bar{V}_2 = V_1^0 + 2R\frac{\partial}{\partial P}(T\Delta B_\rho \rho_1^0),$$

entropy

$$\bar{S}_{2,aq} = (S_{2,g}^0 - S_{1,g}^0) + S_1^0 + \tilde{R}\ln 55.51 - 2\tilde{R}\frac{\partial}{\partial T}(T\Delta B_\rho \rho_1^0),$$

and heat capacity

$$\bar{C}_{p2} = (C_{p2,g} - C_{p1,g}) + C_{p1}^0 - 2\tilde{R}T\frac{\partial^2}{\partial T^2}(T\Delta B_\rho \rho_1^0),$$

where as above index '$_g$' stands for ideal gaseous component at given temperature and standard pressure, and index '$_1$' stands for the solvent.

Temperature dependence of ΔB_ρ was proposed in the form

$$\Delta B_\rho = \frac{10^3}{T}\left[\beta_1\left(1 - \exp\left\{-\beta_2\frac{10^6}{T^2}\right\} + \beta_3\frac{10^6}{T^2}\right)\right],$$

as well as pressure dependence was neglected. Here β_1, β_2, β_3 are the empirical parameters that could be extracted from the experimental data for the Henry's constant.

Now, knowledge of the pure gas thermodynamics together with these three parameters enables oneself to predict the whole set of infinite dilution thermodynamic properties of the solute at wide range of temperatures (0–500°C) and pressures (1–2000 bar) including the near critical region. The β-parameters for geochemical important aqueous non electrolytes (CO_2, CH_4, H_2S) were extracted. As an example accordance between experimental data and theoretical predictions for the dissolved H_2S is illustrated in Fig. 1.

The proposed approach could also be used to estimate the concentration dependencies of the non electrolytes' thermodynamic properties.

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References

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