# Speciation and mineral equilibria in the mixed natural fluids H$_2$O−non polar gas

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Fluid inclusion analyses indicate that natural fluids rich with dissolved non polar gases (up to 30 mole percent of $CO_2$, $N_2$, $CH_4$) are widespread and play an important role in the genesis of different types of ore deposits. Physical chemistry of such fluids may be rather unconventional with comparison to the 'traditional' pure aqueous solutions. One of the main cause of the distinction is specified in the pronounced lowering of dielectric constant of the mixture because of non polar gas presence. A method tot account of this effect in mixed fluids on ionic and phase equilibria is proposed.

The method is based on consistent account of solvation effects of every aqueous species, that in terms of the well known HKF equation of state (Tanger and Helgeson, 1988) refers to the modification of its chemical potential because of the change of dielectric constant of the mixed solvent, $\varepsilon$, compared to that of pure water, $\varepsilon_{H_2O}$

$$\Delta\mu = \omega \cdot \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{H_2O}} \right),$$

where $\omega = 1.66027 \cdot 10^5 Q^2/r_e$ is the Born parameter of an ion with charge $Q$ and electrostatic radius $r_e$. Thus the proposed method may be considered as a expansion of the revised HKF model for the case of mixed (H$_2$O-non polar gas) fluid. On the other hand usage of the HKF format and thermodynamic database *SUPCRT92* (Johnson *et al.*, 1992) enables oneself not to confine within examination of isolated reactions, but study equilibria of the whole system. Volumetric properties of the mixtures were calculated on the base of Redlich-Kwong equation of state. The traditional range of its application was extended to the low temperature region (down to 100°C) and the infinite dilution conditions. The proposed modification is essentially based on the usage of the *exact* multiparametric unified equation of state for H$_2$O given by Hill (1990). Method also includes procedure for computation various thermodynamic

properties of the dissolved gases in wide temperature (25−800°C) and pressure (1−6000 bar) range.

The dielectric constant $\varepsilon$ of the mixture was calculated with use of the modified Kirkwood equation

$$\frac{V}{4\pi N_{Av}} \cdot \frac{(2\varepsilon + 1)(\varepsilon - 1)}{3\varepsilon} = x_{gas} \cdot \alpha_{gas} +$$

$$x_{H_2O} \cdot \left( \alpha_{H_2O} + \frac{2.4143 \cdot 10^{-21} \cdot d_{H_2O}^2 \cdot g}{T} \right),$$

where $V$ is the molar volume of the mixture, $x_{H_2O}$, $\alpha_{H_2O}$ and $x_{gas}$, $\alpha_{gas}$ are the mole fractions and polarizabilities of H$_2$O and the gas, respectively, $d_{H_2O}$ is the electric dipole moment of the H$_2$O molecule, and $g$ is the 'Kirkwood correlation factor' that represents the orientation of the neighbouring molecules due to the hydrogen bonds. It is to stress, that $g$-factor is calculated for pure water using a value of the *whole* volume $V$ instead of the *partial volume* $\bar{V}_{H_2O}$ in the mixture. As it was remarked by Orlov and Smirnov (1994) such an approach is applicable for mixtures H$_2$O-non polar component where the interaction between dissimilar molecules can be neglected. The validity of the equation for $\varepsilon$ was justified while comparing the predicted and the available experimental data for H$_2$O-dioxane mixtures at temperature range 0−80°C and H$_2$O-benzene mixtures at 300−400°C under pressures from 100 to 2800 bar.

Activity coefficients for charged species were calculated using the Debye-Hückel equation and that for the neutral species were set equal to unity. The solubility and dissociation calculations were performed with the use of a modified version of the *BALANCE* computer code for computing equilibria in multi-component systems. The *SUPCRT92* code (Johnson *et al.*, 1992) was included in *BALANCE* as a subroutine.

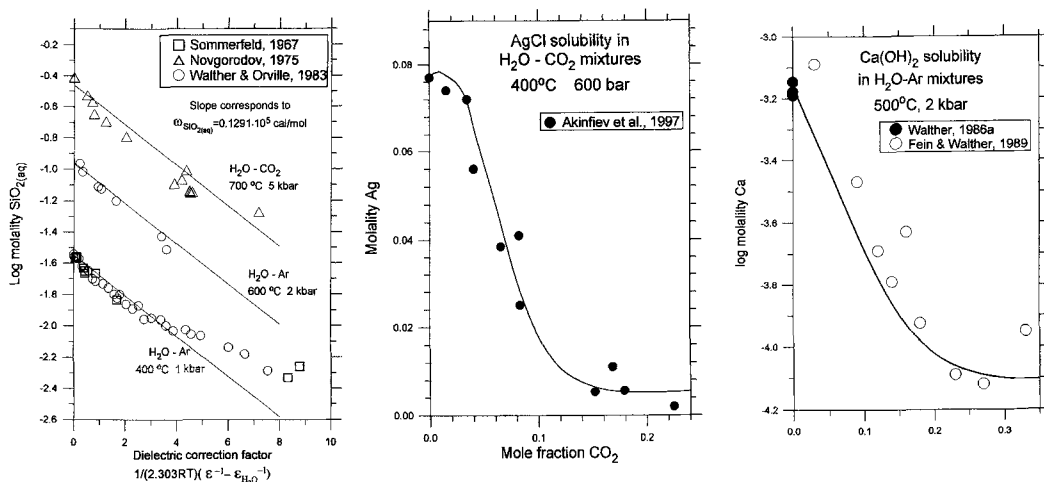The proposed approach has been validated by

FIG. 1. Solubilities of quartz $SiO_2$, chlorargyrite AgCl, and portlandite $Ca(OH)_2$ in the mixed fluids. The symbols represent experimental data, the lines correspond to theoretical prediction.

processing the available experimental data on dissociation constants of $H_2O$ and NaCl and solubility of both covalent and ion crystals ($SiO_2$, AgCl, $Ag_2SO_4$, $Ca(OH)_2$, $CaCO_3$) in mixtures of $H_2O$ and non polar component (dioxane, Ar, $CO_2$). Predicted and experimental data are in close agreement over a wide range of $P-T-x_{gas}$ conditions (up to 700°C, 5 kbar and $0.25-0.3$ mole fraction of non polar gas). Some of them are illustrated in the figure.

It is also shown that the computation method can be applied for estimation the Born parameters of aqueous species. The extracted data for Ca-complexes are presented in Table 1.

TABLE 1. Thermodynamic properties of Ca complexes extracted in this study

| Thermodynamic parameters | | $CaOH^+$ | $CaHCO_3^+$ |
|---|---|---|---|
| $\delta_f G^0_{298}$ | cal/mol | $-171490$ | $-273720$ |
| $S^0_{298}$ | cal/mol/K | $-5.346$ | $8.003$ |
| $C_{P,298}$ | cal/mol/K | $15.59$ | $67.408$ |
| $V_{298}$ | cm³/mol | $-29.4$ | $4.764$ |
| $a_1 \cdot 10$ | cal/mol/bar | $-2.2875$ | $2.448$ |
| $a_2 \cdot 10^{-2}$ | cal/mol | $-13.3704$ | $-1.826$ |
| $a_3$ | cal·K/mol/bar | $11.0053$ | $6.468$ |
| $a_4 \cdot 10^{-4}$ | cal·K/mol | $-2.2263$ | $-2.7035$ |
| $c_1$ | cal/mol/K | $14.5527$ | $55.5203$ |
| $c_2 \cdot 10^{-4}$ | cal·K/mol | $0.1431$ | $6.1746$ |
| $\omega 10^{-5}$ | cal/mol | $-0.082$ | $0.0723$ |

## References

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