On the problems of calculating the solubility of metal oxides in the vapor phase of water

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In the metal oxide-water systems available thermodynamic data for gaseous hydroxides predict the vapor phase solubility values, which are several orders of magnitude lower than the experimental determinations. An approach to solving this problem by incorporating the quantum-chemical calculations of the hydrated form of gaseous hydroxides is proposed.

Key words: solubility, quantum-chemical calculations, the thermodynamic properties of the ideal gas

A number of investigators on the basis of studies of gas-liquid inclusions, analyzes of fumarolic gas condensates and experimental studies have shown that the vapor phase of hydrothermal solutions is able to transfer significant amounts of metalloids (B, Si, Ge, As, Sb, Te, etc.) and even metals (Mo, Ag, Cu, Au). Available to geochemists thermodynamic databases do not allow to predict the behavior of these metals in the low-density fluids with sufficient accuracy. Thus, the determination of the speciation of the elements in the vapor phase and their thermodynamic properties is an important task of modern geochemistry of hydrothermal processes.

The analysis should begin with those forms, which always exist in the presence of water, i.e. with the oxide and hydroxide species. For a number of metalloids the stoichiometry of the species have been determined spectroscopically – these are hydroxides (i.e. $As(OH)_3$, $B(OH)_3$, $Si(OH)_4$, etc.).

The thermodynamics allows calculating the values of the solubility of oxides in steam, if the thermodynamic properties of the hydroxides in the ideal gas state and their fugacity coefficients $\phi_2^\infty (T, P)$ as a function of temperature and pressure are known. For the dissolution reaction $MeO(s) + nH_2O(g) = MeO \cdot (H_2O)_n(g)$ at given T и P the following expression for the equilibrium constant is valid:

$$\ln K^\circ(T) = \ln \frac{Y_2 \cdot (P/P^\otimes)\phi_2^\infty}{(f_1)^n} - \frac{V(MeO(s)) \cdot (P - P^\otimes)}{RT},$$

where Y_2 designates the mole fraction of a metal in the vapor phase, f_1 stands for the fugacity of pure water, ϕ_2^∞ is the fugacity coefficients of the dissolved species at its infinite dilution in water, V represents the molar volume of a solid phase, $P^\otimes = 0.1$ MPa is the standard pressure.

The values of K° can be calculated from the thermochemical data with the relation $-RT \ln K^o = g_T(MeO \cdot (H_2O)_n(g)) - g_T(MeO(s)) - g_T(H_2O(g))$, where g_T is the Gibbs energy of a compound at the standard pressure. Note that, as a rule, the thermodynamic properties of the hydroxides in the ideal gas state are unknown. The evaluation of the fugacity coefficients of the dissolved hydroxides in the present work is done according to the equation that follows from the virial equation of state [*Prausnitz et al., 1999*]:

$$\ln \phi_2^\infty = \frac{2B_{12}}{V_1} - \ln \frac{PV_1}{RT},$$

where B_{12} is the second mixed virial coefficient for the gas-phase interaction between a hydroxide and water, and V_1 stands for the molar volume of pure water. In the current work, the estimation of B_{12} is made using the relation $B_{12} \approx k \cdot B_{11}$, where B_{11} is the second virial coefficient of water [*Harvey and Lemmon, 2004*], and k is assumed to be equal to the number of hydroxide groups and oxygen atoms in the molecule of a dissolved oxide or hydroxide.

As an example, Fig. 1 shows the values of the solubility of quartz in the vapor phase of water for a number of pressures, calculated under the assumption of the existence of a single form $Si(OH)_4(g)$, in comparison with the available experimental data. The required values of the thermodynamic properties of $Si(OH)_4(g)$ are taken from [*Plyasunov, 2011*]. As can be seen, the agreement between the experiment and calculation is quite satisfactory.
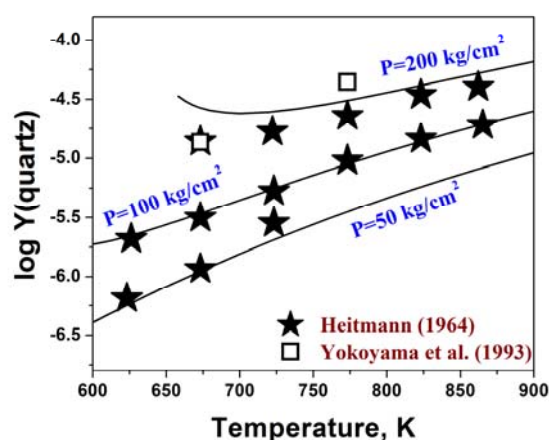
Fig. 1. The experimental and calculated values of the solubility of quartz in the vapor phase of water

At the same time, the calculated solubility of ZnO(s) in steam at 623 K under the assumption of the formation of a single form $Zn(OH)_2(g)$, shown by the dashed line in Fig. 2, is an order of magnitude lower than the experimental value at 16 MPa [*Bénézeth et al., 2002*].
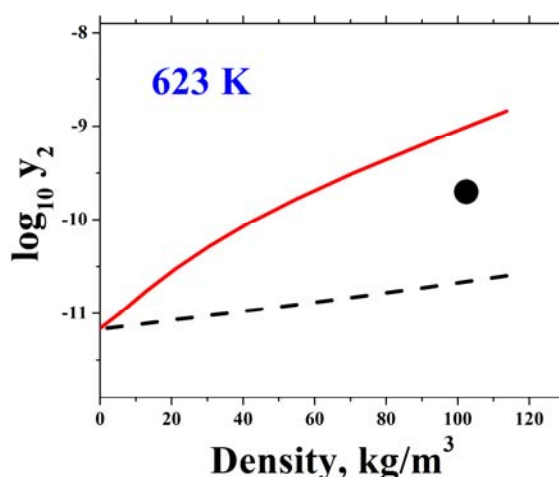
Fig. 2. The calculated values of the solubility of ZnO(s) in the vapor phase of water at 623 K in comparison with the experimental value at 16 MPa [*Bénézeth et al., 2002*]. The dashed line shows the calculated values, obtained under the assumption of the formation of a single form $Zn(OH)_2(g)$, and the

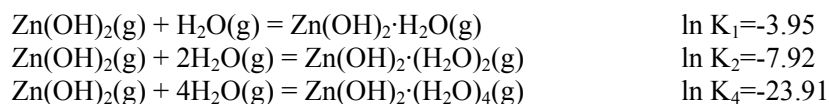solid line corresponds to the calculation with the formation in steam of $Zn(OH)_2(g)$, $Zn(OH)_2 \cdot H_2O(g)$ и $Zn(OH)_2 \cdot (H_2O)_2(g)$

One possible reason for discrepancies between the experiment and calculations is that it is necessary to take into account the existence of clusters in the vapor phase, such as $Me(OH)_n \cdot (H_2O)_m$. Thus the task is to calculate by the quantum chemistry methods the thermodynamic properties of such clusters in the ideal gas state over a wide temperature range, and on this basis, to evaluate the relative stability constants of these clusters.

Quantum chemical calculations were based on the density functional theory (DFT) with the hybrid functional B3LYP and a set of basic wave functions 6-311G+(d,p) for the "light" atoms (A <79 g mol^{-1}) and using the effective core potential LANL2DZ for A > 79 g mol^{-1}.

The calculations resulted in the thermodynamic description of some compounds $Me(OH)_n \cdot (H_2O)_m$ in the ideal gas state over a wide temperature range (273–1273 K).

For the ZnO–H$_2$O system, such calculations were performed for gaseous clusters of the compositions $Zn(OH)_2$, $Zn(OH)_2 \cdot H_2O$, $Zn(OH)_2 \cdot (H_2O)_2$ and $Zn(OH)_2 \cdot (H_2O)_4$. For the consecutive reactions of hydration of zinc hydroxide in the gas phase, the following values of equilibrium constants at 623 K were obtained:

$$Zn(OH)_2(g) + H_2O(g) = Zn(OH)_2 \cdot H_2O(g) \qquad \ln K_1 = -3.95$$
$$Zn(OH)_2(g) + 2H_2O(g) = Zn(OH)_2 \cdot (H_2O)_2(g) \qquad \ln K_2 = -7.92$$
$$Zn(OH)_2(g) + 4H_2O(g) = Zn(OH)_2 \cdot (H_2O)_4(g) \qquad \ln K_4 = -23.91$$

The distribution of zinc forms depending on the density of steam at 623 K is shown in Fig. 3, left.
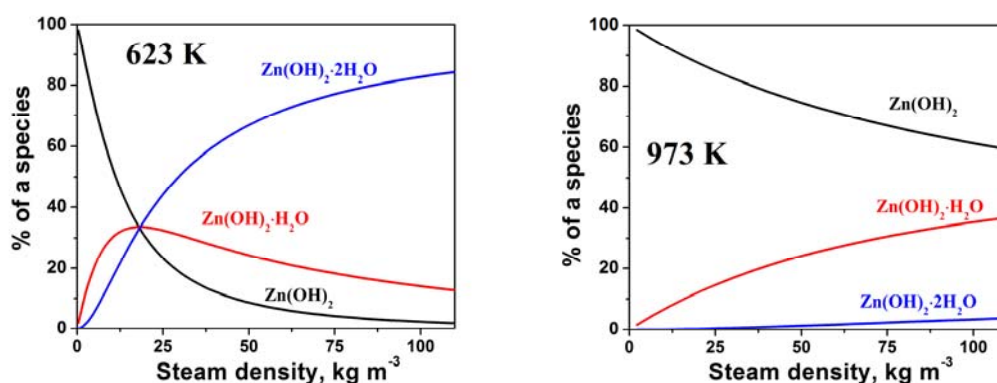
Fig. 3. The distribution of zinc forms in steam at 623 K (left) and 973 K (right) depending on the water density

Clearly, at 623 K the unhydrated hydroxide predominates only at very low densities of steam ρ_1, at intermediate values of ρ_1 the fraction of monohydrate $Zn(OH)_2 \cdot H_2O$ is appreciable, and at the water densities above 25 kg m^{-3} dihydrate $Zn(OH)_2 \cdot (H_2O)_2$ dominates absolutely. The contribution of tetrahydrate is negligible at these conditions. The consideration of all forms significantly increases the calculated solubility of ZnO(s) in steam at 623 K (see the solid line in Fig. 2).

According to calculations, the distribution of zinc forms in steam depends strongly on the temperature, and the dehydration of the species with the increasing temperature is obvious. For example, with the increase of the temperature to 973 K the predominant form of zinc becomes the unhydrated hydroxide, over the entire range of considered vapor densities, 0–100 kg m^{-3} (Fig. 3, right).

Conclusions

The analysis of transport processes of compounds in the gas phase requires the knowledge of the stoichiometry of forms and their thermodynamic properties.

The methods of quantum chemistry allow calculating thermochemical properties of various forms of the type $Me(OH)_n \cdot (H_2O)_m$ in the ideal gas state and evaluating their relative stability.

The application of these methods to the Me-O-H systems showed that in the gas phase not only hydroxides are stable, but also hydrates of hydroxides, and in many cases, the contribution of hydrates is predominant.

The consideration of all forms of metals greatly increases the calculated solubility of the compounds in the vapor phase, often improving the agreement between the experimental and calculated values.

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