

Potentiometric studies of zinc oxide solubility to high temperatures

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Experiments involving metal hydroxide/oxide solubilities imply exact control and quantitative measurement of numerous critical variables such as temperature, pH, metal ion concentration, pressure, ionic strength, oxygen fugacity, etc. Perhaps the most difficult parameter to measure (and/or estimate) is pH, but in the present study pH was measured directly by employing a hydrogen-electrode concentration cell (HECC), which provided continuous *in situ* monitoring of hydrogen ion molality. This cell has been recently used to measure the solubility of minerals such as brucite, boehmite, zincite, and magnetite. Among these minerals, the solubility of zincite (ZnO) has been measured using the HECC in order to determine the thermodynamic properties of aqueous zinc species. Although many ZnO solubility experiments have been performed in alkaline media (e.g. Khodakovskiy and Yelkin, 1975; Plyasunov *et al.*, 1988; Ziemniak *et al.*, 1992) and more recently in acidic solutions (e.g. Wesolowski *et al.*, 1998), no accurate measurements have been made to determine the thermodynamic properties of intermediate zinc hydrolyzed species. Also, a disparity exists in the prediction of their thermodynamic properties due to the sparse data sets reported in the literature.

Experimental procedure

The hydrogen-electrode concentration cell (HECC) consists of a pressure vessel containing two concentric Teflon cups separated by a porous Teflon plug, which acts as a liquid junction completing the electric circuit. Teflon-insulated platinum wires coated with platinum black protrude into each cup and serve as electrodes. The solution in the inner cup serves as the reference of known hydrogen ion molality, whereas the outer, or test, solution contains a suspension of zincite. Solution samples can be withdrawn from this cell for analysis of zinc content by ICP, AA (graphite furnace and flame). Acidic or basic titrant (at matching ionic strengths) can be metered independently into the test cell to change the pH after attainment of equilibrium

(within *c.* 12 hours) so that the entire solubility profile can be mapped out.

Results and discussion

The solubility of pure ZnO has been measured in noncomplexing solutions over a wide range of pH (5–11), temperature (25–290°C), at an ionic strength of 0.03 molal NaTr (sodium trifluoromethanesulfonate). As an example, Fig. 1 shows the results of multiple titrations obtained at 100°C performed both from the acid and base side using the appropriate titrant. These results show that solubility of zincite is reproducible and also reversible, because the same zinc concentration is obtained from both over- and undersaturation. The solid curve in this figure represents the solubility calculated from a fit of the data using a general least-squares program.

The treatment of the experimental data shows that only monomeric species are involved and that 4 species (Zn^{2+} , $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2^0$ and $\text{Zn}(\text{OH})_3^-$) are needed to fit the data at each temperature investigated. Previous authors reported an additional

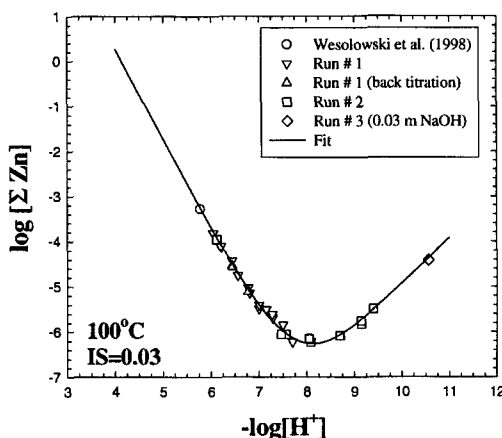


FIG. 1. Solubility profile of ZnO at 100°C and 0.03 mol.kg⁻¹ ionic strength.

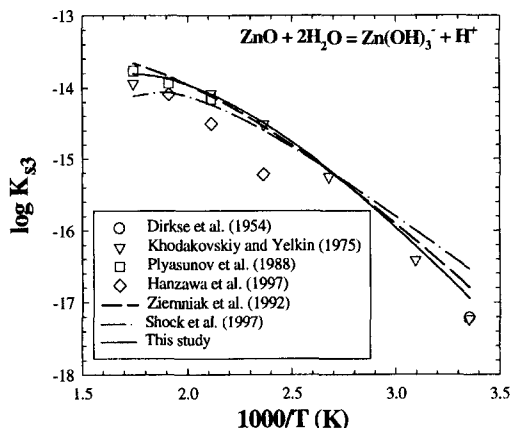


FIG. 2. $\log K_{s3}$ as a function of the reciprocal of temperature.

species in alkaline media, $\text{Zn}(\text{OH})_4^{2-}$, which was not detected in our experiments, because high hydroxide concentrations were not achievable in the low constant ionic strength media used.

In order to compare our results with the literature data, the dissociation quotients (Q_{sn}), obtained at 0.03 molal ionic strength, were corrected to infinite dilution using an extended Debye-Hückel expression.

The values we obtained are in good agreement with most of the previous results for Zn^{2+} and $\text{Zn}(\text{OH})_3^-$ (see Fig. 2 for example), but disagree with virtually all previous studies for the intermediate species, as can be seen in Fig. 3 for the example of $\text{Zn}(\text{OH})_2^0$.

The discrepancies arise mainly because the previous experiments were performed: 1) in alkaline to near-neutral media and were therefore unable to evaluate accurately the thermodynamic properties of $\text{Zn}(\text{OH})^+$ and $\text{Zn}(\text{OH})_2^0$; and 2) at temperatures ranging mostly from 100 to 350°C, then extrapolated to 25°C. However, we have observed that precipitation of a metastable solid phase, $\text{Zn}(\text{OH})_{2(s)}$, on ZnO surface, associated with higher solubilities, occurs for temperatures higher than 200°C in near neutral media. The formation of this solid phase was checked by various spectroscopic measurements (e.g. XPS, Raman,...). For this reason, only the experimental constants obtained in the range 75 to 200°C for the intermediate hydrolyzed species were taken into account in our fitting procedure, as represented by the solid curve in Figs. 2 and 3. No significant temperature dependence exists for the neutral species as observed also in the case of $\text{Al}(\text{OH})_3^0$ species over this temperature range.

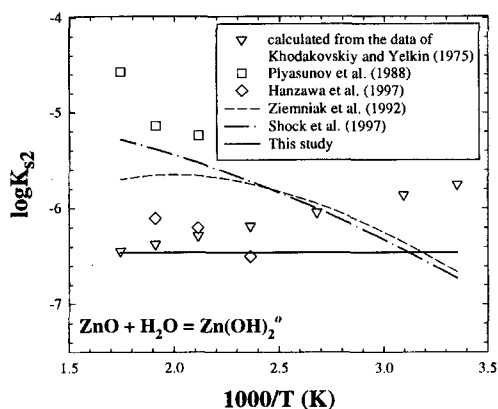


FIG. 3. $\log K_{s2}$ as a function of the reciprocal of temperature.

Conclusions

The HECC has provided *in situ* high-temperature (to 290°C) measurement of pH in a solubility experiment. This approach has been applied to the study of heterogeneous reactions, including adsorption of H^+ / OH^- on oxide surfaces and is entirely amenable to studies of the kinetics of aluminosilicate dissolution/precipitation, and the corresponding equilibrium solubilities, as well as to the rates and equilibrium constants of mineral transformation reactions.

Acknowledgements

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