

## SOLUBILITY OF NICKEL OXIDE AND HYDROXIDE IN WATER

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The solubility of  $\text{NiO}_{(\text{cr})}$  was measured using flow techniques and a potentiometric method from 0 to 350°C in aqueous solutions as a function of pH. A more limited study of the solubility of  $\beta\text{-Ni}(\text{OH})_{2(\text{cr})}$  was conducted by both techniques to 200°C. These results indicate that the transition temperature at which nickel hydroxide dehydrates to form the oxide is *ca.* 75°C, much lower than previously reported. However,  $\beta\text{-Ni}(\text{OH})_{2(\text{cr})}$  can persist as a metastable phase to 200°C for a sufficient period of time to conduct solubility measurements. The oxide was also found to persist to below ambient temperatures, at least in acidic solutions. Independent calculations of the thermodynamic properties of these two nickel phases support the claim of a 75°C transition temperature.

The principal equilibria to be considered for the example of  $\text{NiO}_{(\text{cr})}$ :



There were two major studies of the solubility of bunsenite,  $\text{NiO}_{(\text{cr})}$ , to high temperatures ( $\leq 300^\circ\text{C}$ ) in the 1980's [1,2]. These results tend to diverge at pH values where mainly  $\text{Ni}(\text{OH})_2^0(\text{aq})$  is dominant in solution above 150°C, which was also thought to be near the lower thermal stability limit of  $\text{NiO}_{(\text{cr})}$ . Tremaine and LeBlanc reported solubility constants for equilibria (1-4), whereas the experiments of Ziemniak *et al.* dealt with the pH region where equilibria (3,4) were believed to dominate. In the current study, despite the wide range of pH investigated, only solubility constants for equilibria (1,3) could be extracted from the data. Nevertheless, the values for  $K_{s0}$ , Eq. (1), are in excellent agreement with those presented previously [1,2], whereas the values of  $K_{s2}$ , Eq. (3), are intermediate between those reported earlier. However, the absence of any anionic Ni(II) species leads to markedly different predicted solubilities at high pH.

There is a huge disparity of almost three orders of magnitude in the solubilities of  $\beta\text{-Ni}(\text{OH})_2$  reported at 25°C over the last 77 years.[3]

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### References

- [1] P.R. Tremaine and J.C. LeBlanc, *J. Chem. Thermodynamics*, **12**, 521-538 (1980).
- [2] S.E. Ziemniak, M.E. Jones, and K.E.S. Combs, *J. Solution Chem.*, **18**, 1133-1152 (1989).
- [3] H. Gamsjäger, H. Wallner and W. Preis, "*Monatshefte Chem.*", **133**, 225-229 (2002).

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