

## RELATIVE SOLUBILITIES OF CORUNDUM, GIBBSITE, BOEHMITE, AND DIASPORE AT STANDARD STATE CONDITIONS: AN ADDENDUM

**Key Words**—Aluminum, Boehmite, Corundum, Diaspore, Gibbsite, Solubility.

In 1988, Peryea and Kittrick reported that acid pretreatment of corundum, gibbsite, boehmite, and diaspore resulted in lower measured solubilities than those obtained for similar samples that were not pretreated with acid. They suggested that this effect was the result of the removal of reactive surface coatings by the acid treatment. Gibbs free energies were calculated for these phases from the solubility data and from the value for the free energy of formation of  $\text{Al}^{3+}$ ,  $-489.4$  kJ/mole, given by Hemingway *et al.* (1978). The resulting free energies of formation were 1.8 to 12.4 kJ/mole more negative than values calculated for untreated mineral samples. The free energies calculated by Peryea and Kittrick (1988), however, may contain a systematic error, because they result in a redefinition of the free energy of formation of gibbsite, the value upon which the free energy of formation of  $\text{Al}^{3+}$  is based.

If the measurements of Peryea and Kittrick (1988; also see Bloom and Weaver, 1982) are to be preferred over those of Kittrick (1966) and Singh (1974), the procedure followed by Hemingway *et al.* (1978; also see Hemingway and Robie, 1977) to calculate the free energy of formation of  $\text{Al}^{3+}$  must be modified. Hemingway *et al.* (1978) calculated the free energy of formation of  $\text{Al}^{3+}$  based upon the free energy of gibbsite calculated from calorimetric measurements of the enthalpy of formation and entropy, using solubility data for gibbsite from Kittrick (1966) and Singh (1974). Therefore, if the solubility of gibbsite reported by Peryea and Kittrick (1988) is to be preferred over earlier measurements of the solubility of gibbsite, the value for the free energy of formation of  $\text{Al}^{3+}$  must be recalculated.

Following the procedures of Hemingway *et al.* (1978) and using the solubility data for gibbsite from Peryea and Kittrick (1988), the revised value for the free energy of formation of  $\text{Al}^{3+}$  should be  $-487.5$  kJ/mole. Based upon this value for the free energy of formation of  $\text{Al}^{3+}$  and the solubility data reported by Peryea and Kittrick (1988) for other aluminum oxide and oxyhydroxide phases, the Gibbs free energies of formation of corundum, diaspore, and boehmite should therefore be  $-1583.7$ ,  $-923.4$ , and  $-919.1$  kJ/mole, respectively. The Gibbs free energy of formation of gibbsite is the reference value and therefore remains unchanged. The revised values for the aluminum oxide and oxyhydroxide phases are at most 1.5 kJ/mole more negative than earlier values.

It is unclear at this time which measured solubility

truly reflects equilibrium with gibbsite and, thus, is the appropriate data set to use in the calculation of the free energy of formation of  $\text{Al}^{3+}$ . Bloom and Weaver (1982) and Peryea and Kittrick (1988) observed a reduction in solubility for acid pretreated gibbsite samples; however, chlorine was present in each solution prior to equilibration, and the decrease in solubility may reflect the effect of an interaction with  $\text{Cl}^-$  rather than the effect of acid pretreatment of the gibbsite sample.

Hemingway (1982, 303–305) reviewed much of the literature on the effect of  $\text{Cl}^-$  in this system. The studies of Hsu (1967) and Frink and Peech (1962) are of particular importance. Hsu (1967) showed that addition of  $\text{Cl}^-$  to hydrolyzed solutions of aluminum had little or no effect, but that  $\text{Cl}^-$  added prior to aluminum hydrolysis retarded precipitation of  $\text{Al}(\text{OH})_3$  phases and caused a change in the phase that precipitated, which suggests that  $\text{Cl}^-$  does indeed alter the normal sequence of aluminum hydrolysis. Frink and Peech (1962) used a single gibbsite sample, but varied the conditions under which solubility experiments were performed. Their results at several values of pH were plotted by Hemingway (1982, Figure 5) together with his interpretation of the equilibrium solubility curve for gibbsite. The measured solubilities from three of the four experimental conditions used by Frink and Peech (1962) appear to lie along three subparallel curves, one of which is consistent with the solubilities reported by Kittrick (1966) and Singh (1974) and the equilibrium solubility curve given by Hemingway (1982), one of which is consistent with the results of Bloom and Weaver (1982) and Peryea and Kittrick (1988), and one of which shows higher solubilities than the other two sets. In the fourth experimental design, HCl was added to a suspension of gibbsite. The latter solutions do not appear to have equilibrated with gibbsite and showed significantly lower aluminum solubility than the results obtained for the other experimental conditions. All of the solutions studied by Frink and Peech (1962) contained  $\text{Cl}^-$ . Those to which HCl had been added showed a lower aluminum solubility than those that contained  $\text{Cl}^-$  as  $\text{AlCl}_3$ . The results of Frink and Peech (1962) that are consistent with those of Bloom and Weaver (1982) and Peryea and Kittrick (1988) had both  $\text{AlCl}_3$  and HCl added to suspensions of gibbsite, and the results that are consistent with those of Kittrick (1966) and Singh (1974) had only  $\text{AlCl}_3$  added to the gibbsite suspension.

The specific effect of HCl on the hydrolysis of alu-

minum is not known at this time; however, the addition of HCl prior to hydrolysis of aluminum clearly can cause a reduction in the observed concentration of aluminum solution species. It is not clear that the lower solubility thus detected represents equilibration between gibbsite and the measured solution species. Therefore, we do not, at this time, recommend a change in the accepted free energy of  $\text{Al}^{3+}$ . We note the problems posed by the results presented by Bloom and Weaver (1982) and Peryea and Kittrick (1988), as well as those of Hsu (1967) and Frink and Peech (1962), and await the results of further studies in these areas.

U.S. Geological Survey  
Reston, Virginia 22092

B. S. HEMINGWAY

College of Agriculture and Home  
Economics Research Center  
Washington State University  
Pullman, Washington 99164

J. A. KITTRICK

Tree Fruit Reseach Center  
Washington State University  
Wenatchee, Washington 98801

F. J. PERYEA

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(Received 15 March 1989; accepted 23 July 1989; Ms. 1891)

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