

The partial molar volume of Fe₂O₃ in alkali silicate melts: Evidence for an average Fe³⁺ coordination number near five

QIONG LIU* AND REBECCA A. LANGE

Department of Geological Sciences, University of Michigan, 2534 C.C. Little Building, Ann Arbor, Michigan 48109-1005, U.S.A.

ABSTRACT

High-temperature (867–1534 °C) density measurements were performed in air on 10 liquids in the Na₂O-Fe₂O₃-FeO-SiO₂ (NFS) system and 5 liquids in the K₂O-Fe₂O₃-FeO-SiO₂ (KFS) system using Pt double-bob Archimedean method. Replicate measurements indicate an average reproducibility of 0.22%. Compositions (in mol%) range from 4 to 18 Fe₂O₃, 0 to 3 FeO, 18 to 39 Na₂O, 25 to 37 K₂O, and 43 to 67 SiO₂. Errors in the gram formula weight are ~0.4%. The molar volumes were fitted to a linear compositional model, which gives a compositionally independent partial molar volume ($\pm 2\sigma$) for the Fe₂O₃ component ($\bar{V}_{\text{Fe}_2\text{O}_3}$) of 41.52 ± 0.34 cm³/mol and zero thermal expansivity. The average residual to the fit is $\pm 0.36\%$ for our 57 measurements on 15 liquids at various temperatures. The value for $\bar{V}_{\text{Fe}_2\text{O}_3}$ in silicate liquids when Fe³⁺ is in fourfold vs. sixfold coordination is estimated to be $\sim 45.5 \pm 1$ vs. $\sim 34 \pm 1$ cm³/mol, respectively. Thus, the fitted value of 41.5 cm³/mol appears to reflect an average Fe³⁺ coordination number between 4.5 and 5.0, which is consistent with recently published X-ray absorption fine structure (XAFS) spectroscopy and molecular dynamics (MD) simulations on Fe³⁺-bearing silicate glasses. In the literature, ^vFe³⁺ is inferred to be present in trigonal bipyramidal sites, in contrast to the square pyramidal sites for ^vTi⁴⁺. The lack of a strong compositional or temperature dependence for $\bar{V}_{\text{Fe}_2\text{O}_3}$ in these alkaline silicate liquids, in contrast to what is observed in the literature for \bar{V}_{TiO_2} in similar melts, may reflect the different geometries for ^vFe³⁺ and ^vTi⁴⁺.