Japan Geoscience Union Meeting 2010
(May 23-28 2010 at Makuhari, Chiba, Japan)

SMP056-P02 Room: Convention Hall Time: May 23 17:15-18:45

Development of oxidative calorimetry method for Fe(II)-bearing silicate samples

Tsukasa Yokoyama[1*], Hiroshi Kojitani[1], Masaki Akaogi[1]

[1]Dept. Cemistry, Gakushuin Univ

Calorimetric measurements of Fe2SiO4 and FeSiO3 have been made several times in recent years. Many of those previous researches were made by the method to dissolve samples into the solvent under an inert gas in the calorimeter kept at high temperature. However, because the samples containing Fe(II) are oxidized easily at high temperature during the experiments, special care should be taken in the experiments. Therefore, in this study, oxidative calorimetry method that positively oxidizes Fe2SiO4 and FeSiO3 was developed, as a more practical calorimetry method. Fe2SiO4 fayalite was prepared from an intimate mixture of Fe2O3 and silicic acid. This mixture was heated at 1453K for 30 hours in mixed-gas flow of H2, CO2, and Ar with volumetric ratios of 1:1:2. FeSiO3 ferrosilite was prepared from a mixture of synthetic Fe2SiO4 and silicic acid. The mixture was held at 5GPa and 1473K for 3hours, using a 6-8 multi-anvil high pressure apparatus. Enthalpies of drop-solution of SiO2 quartz, Fe2O3 hematite, and synthetic Fe2SiO4 and FeSiO3 in molten 2PbO.B2O3 were measured at 978K, using a Calvet-type calorimeter. To oxidize the sample enough during the enthalpy measurement, a bubbling method with pure air was used together.
Measured enthalpies of drop-solution at 978K was -49.9(17)kJ/mol for Fe2SiO4, -4.7(30)kJ/mol for FeSiO3, 38.7(9)kJ/mol for SiO2, and 169.2(59)kJ/mol for Fe2O3. The reaction of Fe2SiO4(298K, solid) + 1/2O2(298K, gas)=Fe2O3(978K, in solvent) + SiO2(978K, in solvent) was calculated from the above drop-solution enthalpies as -49.9(17)kJ/mol in this study, which is consistent with the value of delta H298 of -48.1kJ/mol by Robie and Hemingway (1995). The delta H298 for the reaction Fe2SiO4+SiO2=2FeSiO3 was -1.8(63)kJ/mol in this study, which is consistent with the value of delta H978 of -3.9(18)kJ/mol by Kojitani and Akaogi (1994). Therefore, we conclude that the oxidative calorimetry method that uses the air-bubbling technique is promising as a practical use.

Keywords: Fe(II), fayalite, ferrosilite, oxidative, enthalpies