

## Free energy of formation of zircon based on solubility measurements at high temperature and pressure

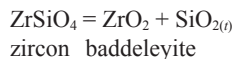
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### ABSTRACT

The standard Gibbs energy of formation of zircon was constrained by measuring the solubility of silica in H<sub>2</sub>O in equilibrium with zircon and baddeleyite at 800 °C, 12 kbar, by a sensitive weight-change method. Dissolution occurs incongruently according to the reaction:



where SiO<sub>2(l)</sub> is total dissolved silica. Blank runs demonstrated that the effects of ZrO<sub>2</sub> solubility and/or capsule-Pt transfer were near the weighing detection limit, so weight losses or gains could be ascribed quantitatively to SiO<sub>2</sub> solubility. Precise SiO<sub>2(l)</sub> concentrations were ensured by use of three types of starting material, by approaching equilibrium from zircon-undersaturation and oversaturation, and by demonstrating time-independence of the measurements. The results yielded a SiO<sub>2</sub> concentration of 0.069 ± 0.002 (1 se) moles per kg H<sub>2</sub>O (*m<sub>s</sub>*), or a mole fraction (*X<sub>s</sub>*) of 1.23 × 10<sup>-3</sup> ± 3.3 × 10<sup>-5</sup>. Two runs on zircon solubility in NaCl-H<sub>2</sub>O solutions at 800 °C and 10 kbar showed silica solubility to decrease by nearly 1% per mol% NaCl.

The standard molar Gibbs free energy of formation of zircon from the oxides at a constant *P* and *T* is given by:

$$\Delta G_{f,ox,zr}^{\circ} = RT \ln \frac{\gamma_s^{ZB} X_s^{ZB}}{\gamma_s^Q X_s^Q}$$

where *ZB* and *Q* refer, respectively, to equilibrium with zircon-baddeleyite and quartz,  $\gamma_s$  is the activity coefficient of total silica, and the relationship between  $\gamma_s$  and *X<sub>s</sub>* accounts for aqueous silica activity. Our results yield  $\Delta G_{f,ox,zr}^{\circ} = -18.5 \pm 0.7$  kJ/mol at 800 °C, 12 kbar (95% confidence), or a standard apparent Gibbs free energy of formation from the elements of  $-1918.3 \pm 0.7$  kJ/mol at 25 °C, 1 bar. Our value is consistent with determinations based on phase equilibrium studies, within reported error limits, but is more precise than most previous values. However, it is less negative than high-temperature determinations by calorimetry and electrochemistry. Our results indicate that solubility measurements at high *T* and *P* may be a superior method of free energy determination of other refractory silicate minerals.

**Keywords:** Experimental petrology, phase equilibria, thermodynamics, zircon