

Equations of state, phase relations, and oxygen fugacity of the Ru-RuO₂ buffer at high pressures and temperatures

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ABSTRACT

Experimental studies and measurements of inclusions in diamonds show that ferric iron components are increasingly stabilized with depth in the mantle. To determine the thermodynamic stability of such components, their concentration needs to be measured at known oxygen fugacities. The metal-oxide pair Ru and RuO₂ are ideal as an internal oxygen fugacity buffer in high-pressure experiments. Both phases remain solid to high temperatures and react minimally with silicates, only exchanging oxygen. To calculate oxygen fugacities at high pressure and temperature, however, requires information on the phase relations and equation of state properties of the solid phases.

We have made in situ synchrotron X-ray diffraction measurements in a multi-anvil press on mixtures of Ru and RuO₂ to 19.4 GPa and 1473 K with which we have determined phase relations of the RuO₂ phases and derived thermal equations of state (EoS) parameters for both Ru and RuO₂. Rutile-structured RuO₂ was found to undergo two phase transformations, first at ~7 GPa to an orthorhombic structure and then above 12 GPa to a cubic structure. The phase boundary of the cubic phase was constrained for the first time at high pressure and temperature. We have derived a continuous Gibbs free energy expression for the tetragonal and orthorhombic phases of RuO₂ by fitting the second-order phase transition boundary and *P*-*V*-*T* data for both phases, using a model based on Landau theory. The transition between the orthorhombic and cubic phases was then used along with EoS terms derived for both phases to determine a Gibbs free energy expression for the cubic phase. We have used these data to calculate the oxygen fugacity of the Ru + O₂ = RuO₂ equilibrium, which we have parameterized as a single polynomial across the stability fields of all three phases of RuO₂. The expression is $\log_{10}f_{\text{O}_2}(\text{Ru} - \text{RuO}_2) = (7.782 - 0.00996P + 0.001932P^2 - 3.76 \times 10^{-5}P^3) + (-13\,763 + 592P - 3.955P^2)/T + (-1.05 \times 10^6 - 4622P)/T^2$, which should be valid from room pressure up to 25 GPa and 773–2500 K, with an estimated uncertainty of 0.2 log units. Our calculated f_{O_2} is shown to be up to 1 log unit lower than estimates that use previous expressions or ignore EoS terms.

Keywords: Oxygen fugacity, ruthenium/ruthenium dioxide, experimental petrology, phase relations, equation of state