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Thermal decomposition of rhombohedral $KClO_3$ from 29–76 kilobars and implications for the molar volume of fluid oxygen at high pressures

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ABSTRACT

$KClO_3$ thermal decomposition has been studied from 29–76 kilobars using a multianvil high-pressure device and in-situ energy-dispersive X-ray diffraction and off-line quenching experiments. The rhombohedral form of $KClO_3$ was found to decompose to the B2 form of KCl and O_2 via an orthorhombic $KClO_4$ intermediate over this pressure interval. The decomposition temperature was found to vary only slightly with pressure. The online experiments gave decomposition temperatures between 500 and 580 °C. Further off-line quenching experiments using sealed gold tubes determined the equilibrium decomposition boundary to be 550 ± 15 °C over this pressure range. Unit-cell parameters and volumes were determined for the high-pressure phases of $KClO_3$ and KCl from the diffraction data. The partial molar volume of O_2 was calculated from the difference in the solid volumes. Oxygen fluid volumes were then calculated along the decomposition boundary and vary from 10.6 ± 0.2 cm^3/mol at 29 kbar to 9.6 ± 0.1 cm^3/mol at 76 kbar. These volumes are 30 to 50% less than previous estimates determined from shock wave data, and imply that oxygen can be more easily stored in Earth's mantle and core than previously believed. The thermal equation of state of the B2 form of KCl was investigated online using NaCl as an internal pressure standard. KCl was then used as an internal pressure calibrant for the online $KClO_3$ decomposition experiments. The mechanical behavior of the multianvil high-pressure device was also studied and load vs. force characteristics are presented here.