

# Experimental determination of hydrogen isotopic equilibrium in the system $\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})$ from 3 to 90°C

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Molecular hydrogen ( $\text{H}_2$ ) is found in a variety of settings on and in the Earth from low-temperature sediments to hydrothermal vents, and is actively being considered as an energy resource for the transition to a green energy future. The hydrogen isotopic composition of  $\text{H}_2$ , given as D/H ratios or  $\delta$ , varies by hundreds of per mil from  $\sim -800\text{‰}$  in hydrothermal and sedimentary systems to  $\sim +440\text{‰}$  in the stratosphere. This range reflects a variety of processes, including kinetic isotope effects associated with formation and destruction and equilibration with water, the latter proceeding at fast (order year) timescales at low temperatures ( $<100^\circ\text{C}$ ; e.g., Pester et al., 2018). At isotopic equilibrium, the D/H fractionation factor between liquid water and hydrogen ( $\delta_{\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})}^{\text{D}}$ ) is a function of temperature and can thus be used as a geothermometer for  $\text{H}_2$  formation or equilibration temperatures. Precise and accurate knowledge of equilibrium  $\delta_{\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})}^{\text{D}}$  as function of temperature over the range of environmentally relevant temperatures where liquid water is present is necessary for use in natural systems. Multiple studies have produced theoretical calculations for hydrogen isotopic equilibrium between hydrogen gas and liquid or vapor water. However, only three published experimental calibrations exist in the  $\text{H}_2\text{O}\text{-H}_2$  system: two between 51 and 742°C for  $\text{H}_2\text{O}(\text{g})\text{-H}_2(\text{g})$  (Suess, 1949; Cerrai et al., 1954), and one in the  $\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})$  system for temperatures  $<100^\circ\text{C}$  (Rolston et al., 1976). Despite these calibrations existing, there is uncertainty on their accuracy at low temperatures ( $<100^\circ\text{C}$ ; e.g., Horibe and Craig, 1995).

Here we present a new experimental calibration of the equilibrium hydrogen isotopic fractionation factor for liquid water and hydrogen gas ( $\delta_{\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})}^{\text{D}}$ ) from 3 to 90°C. Equilibration was achieved using platinum catalysts and verified via experimental bracketing by approaching final  $\delta_{\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})}^{\text{D}}$  at a given temperature from both higher (top-bracket) and lower (bottom-bracket) initial  $\delta$  values. Final  $\delta_{\text{H}_2\text{O}(\text{l})\text{-H}_2(\text{g})}^{\text{D}}$  values given by averaged top- and bottom-brackets are in general agreement with previous experimental data and theoretical calculations but exhibit  $\pm 10\text{‰}$  deviations. We will discuss these deviations and the implications of this work on the estimation of formation and re-equilibration temperatures of  $\text{H}_2$  in low-temperature settings on Earth.

