An experimental and theoretical calibration of CH_4-H_2-H_2O hydrogen isotopic equilibrium from 3-200°C

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The hydrogen isotopic composition of CH_4 is used to trace both its provenance and formational mechanisms. Based on CH_4 clumped-isotope measurements, it has been proposed that CH_4 may form in or later reach hydrogen isotopic equilibrium with local waters at temperatures <200°C (e.g., Stolper et al., 2015; Wang et al., 2015; Giunta et al., 2019).

Horibe and Craig (1995) experimentally determined and provide an equation for the relative hydrogen isotopic composition of CH_4 vs. $H_2O_{(l)}$ at equilibrium ($\alpha_{CH4(g)\text{-}H2O(l)}$) from 200-500°C. Below 200°C, $\alpha_{CH4(g)\text{-}H2O(l)}$ can be estimated by extrapolating the Horibe and Craig (1995) equation or using theoretical estimates of $\alpha_{CH4(g)\text{-}H2O(g)}$ (Bottinga, 1969, Richet et al., 1977) combined with experimental determinations of $\alpha_{H2O(g)\text{-}H2O(l)}$ (Horita and Wesolowski, 1994). Such approaches yield $\alpha_{CH4(g)\text{-}H2O(l)}$ values that differ by up to 163‰ at 0°C. Consequently, knowledge of $\alpha_{CH4(g)\text{-}H2O(l)}$ at low temperatures (<200°C) is uncertain.

Here we present an experimental determination of $\alpha_{CH4(g)\text{-}H2O(l)}$ at temperatures <200°C. We equilibrated CH_4 and H_2 from 3-200°C with γ-Al_2O_3 catalysts and converted values of $\alpha_{CH4(g)\text{-}H2(g)}$ to $\alpha_{CH4(g)\text{-}H2O(l)}$ using previous experimental determinations of $\alpha_{H2(g)\text{-}H2O(l)}$ (Rolston et al., 1976) or $\alpha_{H2(g)\text{-}H2O(g)}$ (Suess, 1949; Cerrai et al., 1954) combined with $\alpha_{H2O(g)\text{-}H2O(l)}$ (Horita and Wesolowski, 1994). We use a bracketing approach to demonstrate experiments reached equilibrium. Our experimentally determined $\alpha_{CH4(g)\text{-}H2(g)}$ values agree with new theoretical estimates presented here based on Path Integral Monte Carlo (PIMC) calculations: Regression of experimental vs. PIMC 1000xln($\alpha_{CH4(g)\text{-}H2(g)}$) values from 550 to 1330‰ yields a slope of 1.008±0.011 (1 s.e.) and intercept of -5.1±10.5. At 3°C, our $\alpha_{CH4(g)\text{-}H2O(l)}$ value differs the extrapolation of Horibe and Craig (1995) by 76‰.

Finally, we show that $\alpha_{CH4(g)\text{-}H2O(l)}$ values of marine CH_4 samples with known formation temperatures commonly yield isotopic compositions consistent with formation in isotopic equilibrium using our calibration while freshwater systems do not. We provide a general explanation for this based on the thermodynamic framework given in Valentine et al., (2004).