# KINETICS OF D/H ISOTOPE EXCHANGE BETWEEN H_2 AND H_2O AND POTENTIAL USE OF ISOTOPE GEOTHERMOMETRY ON PLUME DATA FROM ENCELADUS.

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Introduction: Molecular hydrogen (H_2) is a common component of crustal fluids on Earth, produced when water reacts with reduced (e.g., Fe-bearing) silicate minerals. At equilibrium, D/H isotope fractionation between H_2 and H_2O ($\alpha_{W-H2} = [D/H]_{H2O} / [D/H]_{H2}$) is T-sensitive and can be used as geothermometer in that α_{W-H2} values measured in surface discharges can help constrain higher subsurface reaction temperatures [1]. Beyond Earth, H_2 has been observed in the gas/particulate plumes of Saturn's moon Enceladus [2], and, should α_{W-H2} be constrained, geothermometry could prove useful for elucidating the T structure in the liquid (H_2O) ocean beneath the icy shell. However, a measured α_{W-H2} value does not necessarily reflect equilibrium or provide the T of H_2 formation because α_{W-H2} will begin to re-equilibrate if T subsequently changes. This requires knowledge of the D-H exchange kinetics between H_2 and H_2O in order to interpret how an observed α_{W-H2} value fits into the broader T history of the solution.

Experimental Results: We recently presented experimentally derived pseudo-first-order rate constants (k_1, units hrs^{-1}) for H_2 dissolved in liquid H_2O [3], which describe the approach to isotopic equilibrium for the reaction: $H_2 + HDO \leftrightarrow HD + H_2O$. If species concentrations are cast in mols/L (accounting for both T and P), we derive an Arrhenius relationship for a rate constant k (units [L/mole] / hr) that can describe both the results of the liquid-phase experiments and those of earlier gas-phase experiments [4] (figure below, Ea = 52 kJ/mole).
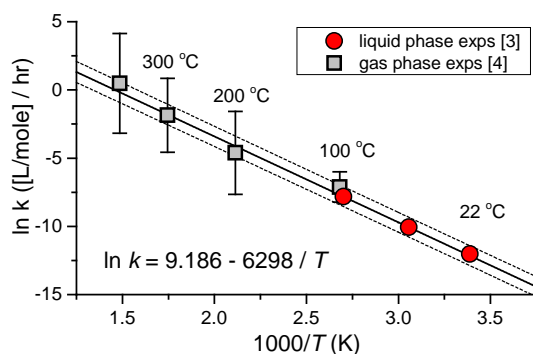
These results infer a density-dependence for the pseudo-first-order constant k_1. In most natural settings $[H_2O] >> [H_2]$, especially when liquid H_2O is present, and $k_1 \approx k[H_2O]$. The phase density therefore strongly influences the equilibration rate, exemplified by $1/k_1$ at 100°C of ~2 days for H_2 dissolved in liquid H_2O, versus ~5 yrs for H_2 in saturated steam.

Discussion: One explanation for the H_2 in the plumes of Enceladus is that it accumulates in the ocean due to ongoing hydrothermal or serpentinization reactions in the rocky core [2, 5]. Application of the geothermometer would assume $[D/H]_{H2}$ in the plumes would be equal to that of H_2 dissolved in the liquid ocean. This is reasonable based on the kinetic data because the plumes discharge at ~400 m/s, and the surface T is -201°C. Regardless of the ocean T and thickness of the ice shell (up to 40 km), this discharge rate is fast enough that no subsequent re-equilibration of $[D/H]_{H2}$ could occur during this process.

Although currently available data are insufficient to calculate an α_{W-H2} value for Enceladus, we can develop preliminary kinetic models to constrain oceanic residence times required for α_{W-H2} to reflect isotopic equilibrium at a likely minimum ocean T of -3°C (i.e. T_{min} at the ice-ocean interface). For example, in one simple model we assume a scenario where water-rock reactions result in the constant addition of new H_2, initially in isotopic equilibrium with a 90°C source water [5], and this source water is instantaneously quenched to T_{min} within a (well-mixed) bulk ocean. Unless there are kinetic isotope effects associated with processes serving as a sink for H_2, the model indicates a residence time of ~180 yrs would be required for the bulk oceanic $[D/H]_{H2}$ to re-equilibrate to within 99% of isotopic equilibrium at T_{min}. However, particulate silica in the plumes suggests more vigorous convective processes may bring deeper (hydrothermal) waters up towards the ice-ocean interface on (shorter) timescales of months [5]. If this is indeed the case, then α_{W-H2} measured in the plume could reflect more elevated T.

More detailed models can be developed if sufficiently resolute values of α_{W-H2} are be obtained. Kinetic models applied to terrestrial hydrothermal systems, where maximum reaction T is independently constrained, further allow us to identify when microorganisms are catalyzing D-H exchange.

References: [1] Arnason (1977) *Geothermics*, 5, 75-80 [2] Waite et al. (2017) *Science*, 356, 155-159 [3] Pester et al. (2017) *Goldschmidt Abstracts*, 3128. [4] Lecluse and Robert (1994) *Geochim. Cosmochim. Acta*, 58, 2927-2939. [5] Hsu et al. (2015) *Nature*, 519, 207-210.