# Stable Isotope Investigations of Redox Processes

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Isotopes are a sensitive marker for interfacial redox processes. Measurements of stable isotope abundances in electrochemically active systems demonstrate their promise as markers for information about the kinetics and thermodynamics of reactions, but only to the extent that the isotope fractionation at each step is understood. Here we revisit our previous derivation of an isotope-sensitive kinetic theory for electrochemical reactions far from equlibirum, based on Marcus theory [1,2]. In a new derivation, equilibrium constraints are satisfied, and the isotope-dependence of the pre-exponential factor is incorporated explicitly into the derivation. The result is a predictive framework for the isotope kinetics of reversible electron transfer reactions. We compare our theoretical predictions against measurements of electrochemical isotope effect in metals including Fe, Zn, and Li.
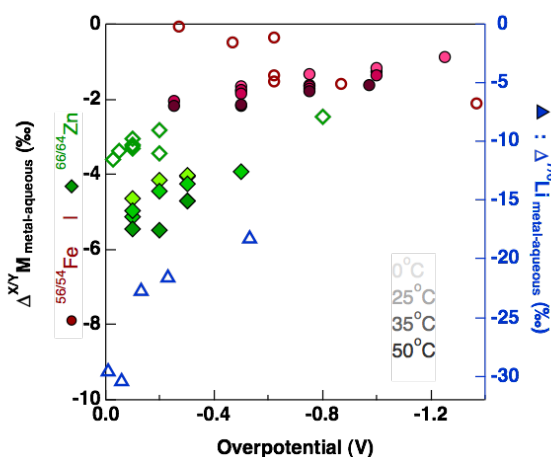


**Figure 1.** Electrochemical isotope fractionation of metals as a function of potential and temperature [3].

[1] Marcus (1965) *J. Chem. Phys.* **43**, 679-701 [2] Kavner *et al* (2005) *GCA* **69**, 2971-2979 [3] Black *et al* (2011) *ACS Symposium Series* **1071**, pp. 345-359