

Modeling Electrochemical Proton-Coupled Electron Transfer Reactions at Metal Electrodes: Spanning Adiabatic and Nonadiabatic Regimes

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A general theory for electrochemical proton-coupled electron transfer (PCET) reactions at metal electrodes will be discussed. The theory can be used to describe redox reactions at the electrode surface coupled to proton transfer in solution as well as the Volmer step of hydrogen evolution reactions where the proton is transferred to a surface active site. The focus of this presentation will be on the adiabaticity of these reactions and general approaches to calculate the potential dependent rate constants and kinetic isotope effects (KIEs). The ultimate goal is to describe the electronically adiabatic, vibrationally nonadiabatic, and vibronically nonadiabatic reactions within the same formalism and obtain rate constant expressions that span the adiabatic and nonadiabatic regimes for the entire range of applied potentials. Illustrative examples of recently studied PCET systems will be discussed, including vibronically nonadiabatic PCET reactions, as well as electronically adiabatic Volmer steps of hydrogen evolution in water with the hydronium ion as a proton donor and in aprotic solvents with bulky amine proton donors.