

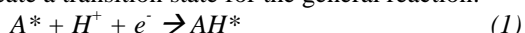
Density functional theory computation of electrochemical activation barriers

Michael J. Janik

Pennsylvania State University, Department of Chemical Engineering
104 Fenske Laboratory, University Park, PA 16803 USA

This talk will address our group's efforts to estimate the potential dependence of elementary electrochemical reaction barriers. Though density functional theory (DFT) studies of electrocatalytic systems are wide spread, the calculation of activation barriers for elementary steps involving electron and ion transfer remains challenging. A simple and transferable method will be presented to estimate these barriers for inner sphere reactions. Example uses of this method will include elementary steps within the oxygen reduction, carbon dioxide reduction, and borohydride oxidation reactions.

Potential dependent activation barriers: The application of DFT methods to evaluate activation barriers for electrochemical steps is challenged by the involvement of ion and electron transfer. In typical DFT approaches for determining activation barriers, a transition state is located between two states with identical charge and number of electrons. For an electrochemical reaction occurring in acidic solution, we must locate a transition state for the general reaction:

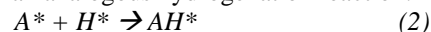


where “*” denotes a surface adsorbed species. A free energy surface for this reaction is illustrated in Figure 1a, with the energy wells for each species approximated as parabolic per Marcus theory. As the reactant state chemical potential involves a proton in the bulk electrolyte (ie, in solution and potentially far from the electrode), and the reaction involves electron motion, it is far from straightforward how to construct a DFT model to locate the desired transition state, and further how to reference this transition state free energy to that of the reactant.

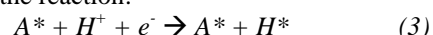
Our approach follows from the assumption that an electrocatalytic elementary step expressed as reaction 1 is inherently an inner-sphere reaction, for which attainment of the transition state requires nuclei rearrangement local to the adsorbed A^* species, and electron transfer is rapid once the nuclei attain the transition state. The Arrhenius concept (transition state theory) of the reaction rate then holds, and the Born-Oppenheimer approximation

allows for evaluation of reaction rates without explicit consideration of electron conduction. These approximations will be valid for reaction 1 if its rate is sensitive to the identity of the catalytic surface. For electrocatalyst development, it is exactly these types of reactions that concern us.

We replace the need to locate a transition state for the electrochemical reaction 1 with the location of a transition state for an analogous hydrogenation reaction:



It is assumed that the transition state for this reaction is identical to the transition state of reaction 1 at one specific electrode potential. Once the transition state is located, the activation free energy for reaction 2, G_{act}^0 , may be assigned to the potential at which the chemical potential of the H^* species is equivalent to the true $H^+ + e^-$ reactant (Fig. 1b). This is done by determining the equilibrium potential, U^0 , of the reaction:



The equilibrium potential, U^0 , is easily determined by established methods popularized by the Nørskov group.

The transition state for reaction 1 and the activation free energy will vary with electrode potential, and the proposed method determines the activation barrier at a single electrode potential. The activation barrier can be extrapolated as a function of electrode potential, U , using Butler-Volmer theory as:

$$G_{act}(U) = G_{act}^0 + \beta F(U - U^0) \quad (4)$$

where F is Faraday's constant. The symmetry factor β , may be approximated as 0.5 (valid for a transition state halfway between reactants and products) or estimated with various approaches.

Applications of this method: We have applied this method to evaluate elementary reaction energetics within the oxygen reduction, carbon dioxide reduction, and borohydride oxidation reaction. Mechanistic conclusions reached from the method will be discussed. In addition to specific mechanistic conclusions, the method can be used to make general conclusions on the preferred paths for reaction classes. We find generally that O-H bonds form (or break) through a transition state indicating that the proton is transferred through solution to the O of the adsorbed species, reflecting a proton-coupled electron transfer process. C-H bonds form (or break) through transition states involving direct H interaction with the surface, resembling more typical heterogeneous catalysis hydrogenation reactions. In addition to detailing these mechanistic conclusions, a series of tests of the dependence of the applied method on reaction trajectory choices, solvation, and interfacial models will be presented.

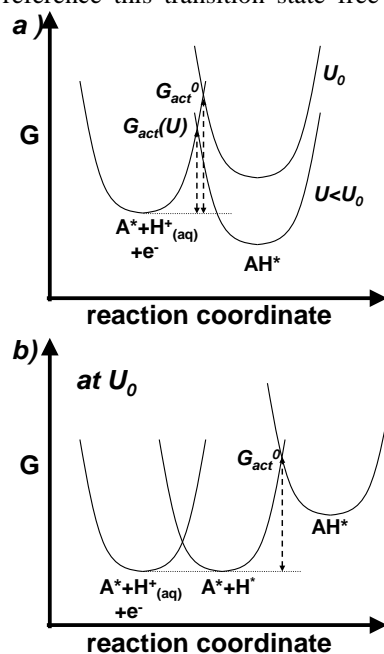


Figure 1. Reaction free energy diagram for a) an electroreduction reaction of an adsorbate A^* . b) schematic reaction energy diagram illustrating the proposed method, where the activation barrier at potential U_0 is determined for the analogous non-electrochemical hydrogenation reaction.