

Tutorial: Electron transfer in electrocatalysis

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All electrochemical electron transfer reactions involve a reorganization of the solvent and an electronic interaction with an electrode, and their energetics are governed by the electrode potential. A useful electron transfer theory must incorporate all of these elements.

We present a model Hamiltonian based on these ideas. It can be treated on various levels. If the electronic interaction between the reactant and the electrode is treated by perturbation theory, we obtain the Levich-Dogonadze-Kuznetsov theory from the late 1960s. If the interaction is somewhat stronger, it makes the reaction adiabatic, but still does not affect the energy of activation – this is the Marcus theory. Both these theories are for outer-sphere electron transfer.

Electrocatalytic reactions are characterized by a strong interaction between the reactant and the electrode, which depends strongly on the distance. For an application of the model to real systems, the various interactions and energies of the model must be obtained from DFT. For this purpose the interactions with the sp- and the d-bands of the electrode must be considered separately. We explain how a d-band situated near the Fermi level can catalyze electron transfer by many orders of magnitude.

We shall discuss several examples such as silver deposition, oxygen reduction, and hydrogen evolution.

References

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