

Kinetic and Thermodynamic Aspects of Voltage as a Driving Force for Ammonia Activation

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Renewable energy sources, such as solar and wind, have become increasingly prevalent and helped drive progress toward decarbonization of electricity. The commodity chemical industry is a large consumer of energy and a major contributor to global greenhouse gas emissions, and electrification of the industry using renewable sources is a possible step toward reducing the carbon footprint of chemicals. In this thesis, I first propose a paradigm where electrochemical systems enable bond-formation steps in the chemical industry, leveraging voltage as an alternative driving force to enable operation at mild temperatures and pressures. I then aim to answer the question “If I can apply mechanical energy (pressure), thermal energy (temperature), or electrical energy (voltage) to a chemical reaction, which should I use?” In particular, I present a universal expression for the equilibrium constant of a chemical reaction as a function of thermodynamic driving forces, and demonstrate how this universal equation and facile visualization of chemical reactions enables quick and informed justification for electrochemical versus thermochemical energy sources.

My thesis focuses on the particular case of electrochemical utilization of ammonia, a ubiquitous nitrogen precursor throughout the chemical industry. In addition to having one of the largest global production rates by volume, ammonia is a key nitrogen source used to synthesize common chemicals such as nitric acid, hydrazine, and cyanide. Moreover, nitrogen functionality in a wide range of chemical products, including nitrogen-containing polymers such as nylon and biochemicals such as amino acids, can often be traced back to either ammonia or reagents that are produced from ammonia. Generally, syntheses for these compounds utilize ammonia in thermochemical reactions, relying on elevated temperatures and pressures as driving forces; in this thesis, I focus on activating ammonia electrochemically using voltage at ambient conditions.

First, I look at an electrochemical analogue to reductive amination, where a carbonyl group is converted to an amine. Specifically, I demonstrate the electrochemical reductive amination reaction of benzaldehyde and ammonia and investigate its kinetics. I find that the reaction proceeds via an inner-sphere route at heterogeneous metal surfaces, in contrast to most previous work on outer-sphere electrochemical reductive amination systems. I then investigate the kinetics of activating ammonia by breaking the nitrogen-hydrogen bond oxidatively, and I find that the reaction proceeds through an outer-sphere, radical pathway. Last, I propose an energy storage paradigm that leverages ammonium formate, a combination of ammonia and formic acid, to store renewable electricity. I discuss the advantages of this fuel and demonstrate how voltage can aid in the release of energy from this fuel. Overall, in this thesis I start with the broad question of why and when to choose electrochemistry over traditional thermochemical routes in the chemical industry, and I then focus in on how electrochemistry can aid in the utilization of ammonia for both synthesis reactions as well as energy storage purposes.

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