Theoretical and modelling concepts in semiconductor defect chemistry and electrochemistry have hugely evolved over the last years and are crucial for their respective fields such as optoelectronics and semiconductor devices or corrosion and battery materials. Recently, we developed an approach which is based on a fully grand-canonical description of both ions and electrons and unifies and “translates” theoretical concepts of these two fields [1]. Our method links ab initio calculations quite naturally to experimental observables such as the pH-scale and the electrode potential, provides surprising new insight into apparently “old” problems such as water stability, opens new routes to construct electrochemical phase (Pourbaix) diagrams, and gives a handle to an absolute alignment of electrochemical potentials. Utilising the gained insight, we discuss the impact an electrochemical environment has on the electronic structure of a semiconducting electrode, by constructing defect stability phase diagrams, which depict the dominant native point defects, for ZnO and water. These enable us to identify areas of interest in the context of electrochemical applications and specify which point defects within the bulk of the semiconducting material will be influenced by the electrochemical environment and impact the properties and stability of the solid [2].
