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The proto electric potential map-unified acidity and reducity scales and their experimental realization

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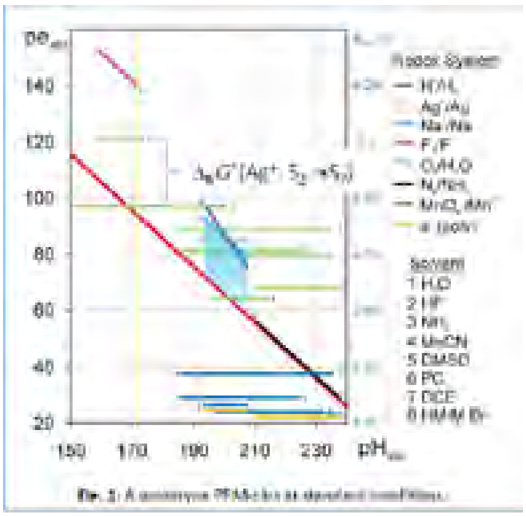
The comparison of acid-base and redox chemistry in their acidity (protonation) and reducity (electronation) scales is currently limited to measurements within one homogenous medium/solvent. Yet, it is crucial being able to measure chemical potentials of the proton and electron over medium boundaries to overcome this limit. Thermodynamically, the chemical potential differences of proton and electron are straightforward to describe, given the unified reference states ideal proton gas (1 bar) and electron gas (1 bar) we suggested in 2010 (proton gas) and 2014 (electron gas). This unifying concept was developed as part of our in March 2017 ceasing ERC UniChem project.

The Proto electric potential map (PPM): In analogy to the proto- and electrochemical window of one medium like water, the PPM is a 2D plot of the medium independent pH_{abs} vs. pe_{abs} values based on these unifying reference states. An example is shown in Figure 1. Any reaction with transfer of protons and/or electrons in any medium may be placed on the PPM. Given that the respective transfer energies are known (see Figure.1), the thermodynamic relations between them may directly be compared over phase and medium boundaries. This plot reveals at a glance the differences of reducity (i.e., electronation power and synonymous to redox potential) of a redox system (marked by colors) in dependence of the solvent S (marked by digits). For example, the Pearson soft de-electronator Ag^+ (green) is up to about 3.5 V or 350 kJ mol^{-1} more effective in hard solvents like HF (2) or DCE (7) rather than in soft media like NH_3 (3) or the Ionic Liquid (IL) HMIM Br (8).

In the lecture, we introduce the concept and present reliable ways to measure the necessary transfer quantities over medium boundaries, e.g., between water and acetonitrile or ionic liquids.



Biography

Ingo Krossing has studied Chemistry in Munich (LMU) and finished his PhD thesis 1997 (with Professor H Nöth). From 1997 to 1999, he worked as Feodor Lynen Post-doctorate with Professor J Passmore at UNB, Canada. In 1999, he started his independent career as a Liebig- and DFG-Heisenberg-Fellow at the Universität Karlsruhe (TH) (Mentor: Professor H Schnöckel). In 2004, he became an Assistant Professor at the Ecole Polytechnic Federale de Lausanne (EPFL), before being appointed as the Chair of Inorganic Chemistry at the Albert-Ludwigs-Universität Freiburg in 2006. His research interests are ionic systems from reactive cations to ionic liquids, as well as electrochemical energy storage. With an ongoing ERC Advanced Grant, he developed absolute acidity and reducity scales.

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