# Critical evaluation of dipolar, acid-base and charge interactions. II. Charge exchange within electrolytes and electron exchange with semiconductors

Jarl B. Rosenholm

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# Critical evaluation of dipolar, acid-base and charge interactions

## II. Charge exchange within electrolytes and electron exchange with semiconductors.

**Jarl B. Rosenholm**
Center of Excellence for Functional Materials
Laboratory of Physical Chemistry at Åbo Akademi University
Porthansgatan 3-5, FI-20500 Åbo (Turku), Finland

## Abstract

Electron displacements may be considered as a general measure of semiconductor activity as well as of dipolar, acid-base and charge interactions. Electron transfers during reduction and oxidation reactions between dissolved cations and anions correspond to an extreme Lewis acid-base electron displacement. Brϕnsted proton release (protolysis) represents an extremely weakened hydrogen bond. The most common electrostatic (Born, PCM) and chemical ($pK_a$ matching) models for electron and proton exchange between dissolved species are reviewed using aluminum species as examples. Dissolution of ions from solids (salts) may be considered as a reversed precipitation reaction. For partly covalent solids dissociation is dependent on electron or vacancy (hole) transfers to the solid which connects oxidation and reduction reactions to electron displacements in semiconductors. The electron exchange is characterized by Femi energy of semiconductors and of electrolytes. The standard reduction potential may thus be converted to Fermi energy of connected electrochemical cells. In disconnected particle suspensions (sols) the electron activity is a more appropriate parameter which may be converted both to standard reduction potential of ions and to Fermi energy of semiconductors. Dissolution of potential determining cations and anions and hydrolysis of surface sites determines the charging (electron transfer to/from surface) of solids. Both electrostatic (MUSIC) and chemical equilibrium constant models are available for Brϕnsted equilibrium of surface hydroxyls. Point of zero charge is a result of positive and negative charge matching and it represents the optimal condition for condensation of polynuclear species by olation and oxolation. The capability of partial charge (PCM) model to predict condensation is evaluated. Acidity ($pH$), composition and temperature dependence of aluminum species is illustrated by solubility limits of contributing species and by phase diagrams. Influence of ions on macroscopic suspension properties, such as wetting and electrophoretic mobility is evaluated with reference to point of zero charge and to isoelectric point. Restrictions to the use of zeta-potentials are related to the surface potential and particle size – Debye length ratios. Macroscopic settling (particle precipitation) and viscosity of suspensions (sols) are discussed with reference to Deryagin-Landau-Verwey-Overbeek (DLVO) model. The primary dependence on counterion valence is evaluated according to Schulz-Hardy approach. The secondary dependence on counterion hydration (Hofmeister or lyotropic effect) and ion association (Debye-Hückel limiting model) are discussed.