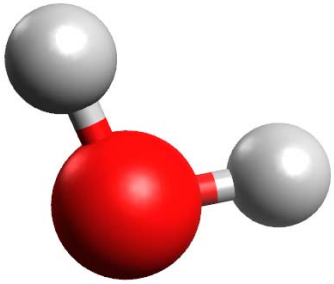
Termodynamikk for metallioner i vandige løsninger fra atomskalamodellering.

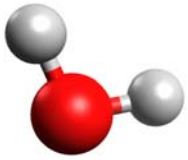


Blindern 16/4 -15

Ole Swang & Francesca Lønstad Bleken

Bakgrunn

- Atomskalamodellering kan gi pålitelige termodynamiske data for et bredt spektrum av systemer.
- Et påfallende unntak er metallioner i vandige løsninger.
- Det er publisert et antall tilnærmelser*
- Det foreligger ikke metodikk som er praktisk, generelt anvendelig.
- En slik metodikk ville ha svært omfattende potensiale:
  - Life science
  - Hydrometallurgi
  - CO_2-fangst
  - Oppstrøms petroleum (scaling)
  - Etc.



e. g. Leung, K.; Rempe, S. B.; von Lilienfeld, O.A. *J. Chem. Phys.* **2009,** *130*, 204507;

Water: You would think that it is simple …

- Liquid water is extremely hard to describe on an atomic level.
  - It's the hydrogen bonds, of course.
- Mesoscale phenomenae: Regions with ice-like structure, with size and lifetime distributions over some 3 orders of magnitude.
- Balance of entropy/enthalpy
- The protons may undergo tunneling
- &c.

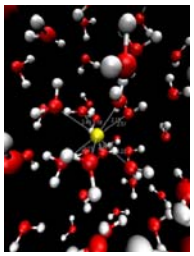
- Fortunately, the solute/solvent interactions are usually simpler!
- An area of intensive research.
- Proof-of concept studies have been published.
- More work is required to make it practically useful.

Issues with water as a solvent

- Proton mobility: Protons, hydroxyl groups, and water molecules swap identities continuously.
- Dynamics!
- High dielectric constant: Ions strongly stabilized.

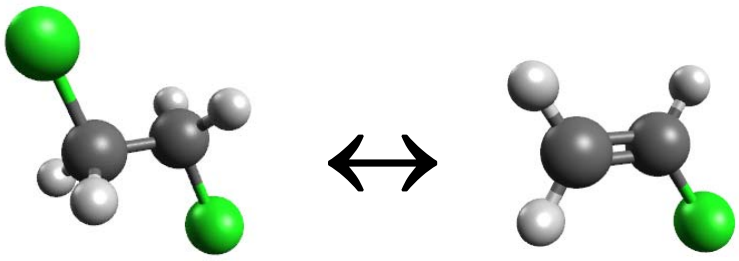
Mål

- Å utvikle og validere *pålitelige, generelt anvendbare* metoder for atomskalabaserte beregninger av Gibbs fri energi for metallioner i vandige løsninger.



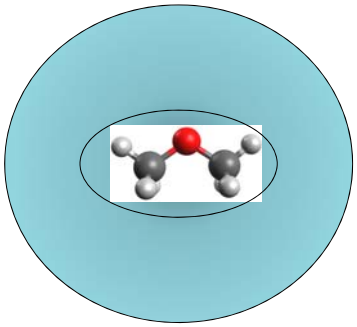
Atom-scale computation of reliable thermodynamics in the gas phase

- Reaction and activation energies accurate to 2 kcal/mol *routinely* available.



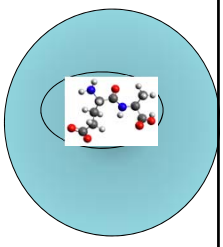
Atom-scale computation of reliable thermodynamics in unpolar solvents

- Reaction and activation energies accurate to 5 kcal/mol routinely available.
- Solute/solvent interactions may be quantitatively calculated with very simplified models
- The solvent is expressed as a dielectric continuum.
- A hole to fit the molecule is taken out of the continuum.



Atom-scale computation of reliable thermodynamics in water

- The method from the prevous slide *usually* works if the ion is large enough (delocalized charge)
- Quasichemical approach: Add a single layer of water molecules between the ion and the continuum.
  - May work for ions that strongly coordinate water.
- Force field based molecular dynamics
  - Good force fields for metals hard to develop
- Ab Initio Molecular Dynamics
  - Very powerful; technically demanding.
- Others



Applications

- Hydrometallurgy
- Waste water treatment
- Life science
- CO_2 capture
- Upstream oil: Scaling, gas hydrates &c.
- Others