Advances in Electrolyte Thermodynamics

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OLI Simulation Conference
2016
Scope

• Structure of OLI’s thermodynamic models
• Progress in thermodynamic modeling
  • Results for selected chemistries
• How predictive can we be?
• Dielectric constant
• Status of databanks
• Plans for the future
## Structure of Thermophysical Property Frameworks

### Aqueous (AQ) Framework
- **Other properties**
  - Electrical conductivity
  - Viscosity
  - Self-diffusivity

### AQ thermodynamics
- **Standard state**: HKF EOS (via fitting equations as default)
- **G\textsuperscript{EX}: Bromley-Zemaitis**
  - \( I < 30 \text{ m}; \ x_{\text{org}} < 0.3 \)
- **Solids**: Equilibrium constants for SLE
- **Gas phase**: SRK equation of state
- **2\textsuperscript{nd} liquid phase**: SRK EOS (same as for gas phase)
- **Interfacial phenomena**: Ion exchange, surface complexation, molecular adsorption

### Mixed-Solvent Electrolyte (MSE) Framework
- **Other properties**
  - Electrical conductivity
  - Viscosity
  - Self-diffusivity
  - Thermal conductivity
  - Surface tension
  - Interfacial tension
  - Dielectric constant

### MSE thermodynamics
- **Standard state**: HKF EOS (direct)
- **G\textsuperscript{EX}: MSE**
  - No concentration limit
- **Solids**: Thermochemical properties
- **Gas phase**: SRK equation of state
- **2\textsuperscript{nd} liquid phase**: MSE G\textsuperscript{EX} model (same as for aqueous phase)
- **Interfacial phenomena**: Ion exchange, surface complexation, molecular adsorption

### Other properties
- **Electrical conductivity**
- **Viscosity**
- **Self-diffusivity**
Progress in Thermodynamic Modeling: Inorganic systems

• Actinide chemistry
  • U(IV, VI), Np(IV, V, VI), Pu(III, IV, V, VI), Am(III), Cm(III)
  • Oxides, hydroxides, carbonates, chlorides, nitrates
  • Redox
  • Surface complexation on MnO$_x$

• Rare-earth element chemistry
  • REE chlorides, sulfates, carbonates, phosphates, hydroxides, acetates, citrates, gluconates

• Transition metal chemistry
  • Ru, Rh, Tc fundamental chemistry
  • Ag nitrate, sulfate systems
  • Ni sulfate systems
Progress in Thermodynamic Modeling: Inorganic systems

• Post-transition metal chemistry
  • Pb silicate, molybdate, tungstate, acetate, formate, nitrate
  • Al nitrate and sulfate with corresponding acids
  • AlF$_3$ - NaF

• Tellurium chemistry
  • Oxides, hydroxides, nitrates, compounds with Na, Zr, Mo

• Silicate chemistry
  • Na aluminosilicates, Ca, Mg, Zn, Al, Pb silicates

• Sodium phosphate chemistry

• Chemistry of solutes in CO$_2$ environments
  • S$^0$, NO$_x$, SO$_x$ in CO$_2$

• High-pressure, high-temperature scaling
  • BaSO$_4$, CaCO$_3$
Progress in Thermodynamic Modeling: Inorganic systems

• C – N – H chemistry
  • Melamine, melam, ammeline, ammelide, cyanuric acid
  • Cyanate chemistry

• Chelant chemistry
  • EDTA and IDA

• Potash chemistry
  • $\text{K}_2\text{SO}_4$ – KCl
  • $\text{Li}_2\text{SO}_4$

• Other salts
  • NaBr
  • Revisions of Sr – SO$_4$ – CO$_2$ chemistry
  • Revisions of FeS and FeCO$_3$ chemistry
Progress in Thermodynamic Modeling: Organic systems

- Hydrocarbon chemistry
  - PVT properties of hydrocarbons
  - Methanol-hydrocarbon systems
  - CO$_2$ – hydrocarbon – H$_2$O systems
  - H$_2$S – hydrocarbon – H$_2$O systems
  - Methane – higher hydrocarbon systems
  - Methane – H$_2$O – salt mixtures

- Organic acid chemistry
  - Maleic acid and anhydride
  - Acetic and formic acids with hydrocarbons

- Monoethylene glycol chemistry refinements
  - PVT properties
  - Effect on SrSO$_4$, FeSO$_4$, FeCO$_3$
Thermodynamics of Actinides

- Trivalent actinides show similar phase behavior
- Weak complexation with Cl⁻
- Moderate increase in solubility due to Cl⁻ complexation
- Model is consistent with both solubility and TRLFS speciation data

Solubility of Am(OH)₃ as a function of pH and Cl⁻

Speciation of Cm(III) as a function of Cl⁻
Thermodynamics of Actinides

- Dual effect of CO$_3$/$\text{HCO}_3$
  - Strong complexation
  - Formation of carbonate solids
How does redox affect solubility?

Behavior of Np(VI)

- Np(VI) is unstable in acidic and neutral environments
- May be easily reduced to Np(V) and Np(IV)

- Solubility and speciation calculated by including redox equilibria
- At near-neutral conditions, Np(V) predominates (red lines) → → → solubility of Np(VI) is governed by reductive dissolution
- At alkaline conditions, Np(VI) predominates (blue lines) → → →
Surface Complexation

Np(V) on hausmanite (Mn₃O₄) in the presence of CO₂

- Double-layer surface complexation model
  - Originally parameterized for hydrous ferric oxide using AQ bulk thermodynamics
  - Applied to actinide sorption on MnO₂ (synthetic, biogenic), MnOOH, Mn₃O₄ using MSE bulk thermodynamics
- Explains relationship between bulk phase and surface speciation
Thermodynamics of Rare Earth Elements

Fundamentals: Phase behavior of LaCl$_3$ – H$_2$O

- DOE’s Critical Material Institute
- Diversifying supply: Improving methods to extract REEs from ores and waste
- Recycling and increasing efficiency of materials use
- OLI’s role
- Provide tools for predicting phase and chemical equilibria to optimize new or improved processes
Thermodynamics of Rare Earth Elements: Application to Bioseparations

- Engineered cell surfaces used to separate REEs from aqueous solutions
- Lanthanide binding tags bind REEs
- Complexing agents are necessary to recover absorbed REEs
- What eluents will work?

Complexation of Tb

- Complexation is necessary to desorb REEs
- Predicted fraction of Tb uncomplexed in solution parallels the observed fraction of Tb that remains bound to the surface

Acetate is inefficient for desorption and Ca interferes with desorption

Small concentration of citrate is sufficient for desorption
Modeling systems containing elemental sulfur

• What are the chemical transformations of SO\(_x\), NO\(_x\), H\(_2\)S, and O\(_2\) in CO\(_2\) transportation pipelines?

• Hence, what are the limits of safe operation?

• Part 1: Model the solubility of S\(^0\) in CO\(_2\)-rich phases in order to predict whether solid S\(^0\) can drop out

• Systems analyzed: Pure S\(^0\), S\(^0\) – H\(_2\)O, S\(^0\) – CO\(_2\)

• Speciation of sulfur
  • Species up to S\(^0\)\(_{20}\) have been detected
  • S\(^0\)\(_1\) through S\(^0\)\(_8\) have been assumed
    • S\(^0\)\(_8\) is dominant at moderate conditions in gas phase
    • Lower multimers become prevalent at higher temperatures
    • In liquid phase, S\(^0\)\(_8\) predominates
    • In CO\(_2\) phase, solvated S\(^0\) – CO\(_2\) species appears
Solubility of $S^0$ in CO$_2$

- Two segments of solubility curves at each T corresponding to gas (or gas-like) and liquid (or liquid-like) CO$_2$.
- Transition is sharp for subcritical CO$_2$ and gradual for supercritical CO$_2$. 

![Graph showing solubility curves](image-url)
Pushing the Limits of Complexity: NaOH + H₃PO₄ + H₂O

- **Temperature range:** to 350°C
- **Chemical equilibria**
  - PO₄⁻³, HPO₄⁻², H₂PO₄⁻¹, etc.
  - Association of Na⁺/H₂PO₄⁻¹
- **Phase equilibria**
  - Vapor-liquid
  - Solid-liquid, sodium pyrophosphate (T > 250°C)
  - **Liquid-liquid** (T > 270°C)
Liquid-Liquid Equilibria at High Temperatures

- Increased ion pairing at high $T$ drives liquid phase demixing
- Lower critical temperature

- LLE depends on the Na/P ratio
- If the solubility drops with $T$, LLE will not appear
How to Deal with Near-Critical Behavior?

- Classical models do not represent near critical behavior
- Crossover models would not be practical for highly speciated reactive systems
- A local model gives a fully quantitative representation of LLE in the high-T region
Modeling Silicates: Importance of Metastable Phases

PbO – SiO$_2$ – H$_2$O

- Multiple competing silicate phases
- Both stable and metastable phases
Mixtures of Hydrocarbons with Acetic Acid

- Reproducing vapor-liquid and liquid-liquid equilibria
- Generalization of parameters for normal alkanes to handle pseudocomponents

LLE for HAc – hexane – H$_2$O ternary

LLE for HAc – hydrocarbon binaries: Miscibility gap increases with carbon number
How Predictive Is the Model?

• Desirable scenario:
  • Develop model parameters based on binary data
  • Predict the behavior of multicomponent systems

• If the model is physically correct, this works
  • Caveat: As long as there is no chemistry change in a multicomponent system
  • Two cases to illustrate predictions
Case 1: Mixed Chloride - Sulfate Systems

- Binary systems
- Regressed parameters
  - Cation-anion interaction parameters
  - Thermochemical properties of solids
- Based on experimental data
  - Solubilities
  - VLE/osmotic coefficients
  - Activity coefficients
  - Enthalpies of dilution
  - Heat capacity
  - Density

\[
\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}
\]

\[
\text{Na}_2\text{SO}_4 \quad \text{(rhombic)}
\]

\[
\text{Na}_2\text{SO}_4 \quad \text{(monoclinic)}
\]

\[
\text{NaCl} \cdot 2\text{H}_2\text{O}
\]

\[
\text{Ice}
\]

\[
\text{NaCl}
\]

\[
\text{NaCl} - \text{H}_2\text{O}
\]

\[
\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}
\]
Case 1: Mixed Chloride - Sulfate Systems

NaCl - Na₂SO₄ – H₂O

- Ternary system
- Regressed parameters
  - Cl⁻ - SO₄²⁻ interactions
  - Second-order correction
  - Binary in nature but obtained from ternary data
- Full complexity of ternary behavior is reproduced
Case 1: Mixed Chloride - Sulfate Systems: Pure Prediction

Behavior of ternary system is accurately predicted without any further parameter adjustment.

Parameters are fully transferable.

No new ternary chemical effects.
Case 2: Mixed Al and Na Salts

- Binary and ternary systems
- Interactions regressed
  - Cation-anion parameters
  - $\text{Al}^{3+}$ - $\text{Na}^+$ cation-cation parameters

![Graphs showing NaF - H$_2$O and AlF$_3$ - H$_2$O systems]
Case 2: Mixed Al and Na Salts

- Although NaF and AlF$_3$ are fairly soluble, solubility in the ternary system AlF$_3$ – NaF – H$_2$O is dramatically lower.
- Specific ternary chemistry effect: Formation of sparingly soluble double salts
  - Cryolite, Na$_3$AlF$_6$, and chiolite, Na$_5$Al$_3$F$_{14}$
- Ternary chemical effects need to be incorporated but cannot be simply predicted from the properties of binary or other ternary systems.
Predicting Dielectric Constant of Mixtures

- Calculating polarization
- Kirkwood theory

\[
\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = p = \frac{4\pi N_A}{3\nu} \left( \alpha + \frac{\mu^2 g}{3kT} \right)
\]

- Mixing rule for polarization

\[
p_m = \frac{\sum_{i} \sum_{j} x_i x_j (vp)_{ij}}{\sum_{i} x_i \nu_i}
\]

\[
(vp)_{ij} = \frac{1}{2} \left( v_i p_i + v_j p_j \right) (1 + k_{ij})
\]

- Good approximation without binary parameters

Monoethylene glycol – water
Predicting Dielectric Constant

- Effect of ionic components

\[ \varepsilon_s = \frac{\varepsilon_{s0}}{1 + \sum_{ions} A_i x_i \ln(1 + B_i \sqrt{I_X})} \]

- Predicts universal decrease with ionic composition

- Effect of ion pairs is more complex

NaCl at 25°C

NaCl at various T
# AQ and MSE Databanks: A Comparison

<table>
<thead>
<tr>
<th>Databank</th>
<th>Aqueous model: Number of species</th>
<th>Mixed-solvent electrolyte model: Number of species</th>
</tr>
</thead>
<tbody>
<tr>
<td>General-purpose (process chemistry)</td>
<td>PUBLIC 5407 (5407 in 10/2014)</td>
<td>MSEPUB 2590 (2150 in 10/2014)</td>
</tr>
<tr>
<td>Geochemical (solids formed on a geological timescale)</td>
<td>138</td>
<td>135</td>
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<tr>
<td>Corrosion (corrosion-related solids)</td>
<td>367</td>
<td>321</td>
</tr>
<tr>
<td>Urea (enabling urea-related reactions)</td>
<td>Not available</td>
<td>8</td>
</tr>
<tr>
<td>Surface complexation, double layer</td>
<td>120</td>
<td>57</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Ceramics (ceramic solids)</td>
<td>36</td>
<td>Not applicable – included in MSEPUB</td>
</tr>
<tr>
<td>Low temperature (extension to calculate properties below 0 C)</td>
<td>227</td>
<td>Not relevant (MSEPUB works below 0 C)</td>
</tr>
</tbody>
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Plans for the Future

• Thermodynamics of rare-earth elements
  • Applications to diversifying the supply, separation and recycling

• High-pressure, high-temperature scaling
  • Solubility of ZnS, PbS and CaSO₄ in produced water environments

• Chemistry of CO₂ transmission
  • Predicting formation of corrosive phases in dense-phase CO₂

• Chemistry of silicates
  • Application to silica removal processes including surface complexation and kinetics
Plans for the Future

• Potash chemistry
  • $\text{K} – \text{Na} – \text{Li} – \text{Ca} – \text{SO}_4 – \text{Cl}$ systems

• Amines and amine hydrochlorides
  • Towards further improvement of predictions

• Finalizing improvements of hydrocarbon chemistry

• Mutual diffusivity
  • Applications to mass-transfer separations

• Future client-driven projects