Hydrothermal Methods for Preparation of Inorganic and Hybrid Materials

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Gypsum (CaSO₄•2H₂O) single crystals in Naica mine, Chihuahua, Mexico
Hydrothermal Synthesis of New Materials

Ag$_4$V$_2$O$_6$F$_2$, a potential Li ion battery cathode

Fe$_3$O$_4$ nanoparticles

IMROF-8, a porous metal-organic framework
Overview of Topics

Definitions
Why use hydrothermal methods?
Equipment and procedures
Chemistry of metal cations in water
Pourbaix diagrams
Examples: Using speciation data to design oxide syntheses
Hydrothermal synthesis of hybrid inorganic-organic compounds
Example: Growing single crystals to characterize corrosion products
Non-aqueous systems
The density, viscosity, and dielectric constant of liquid water decrease as the critical point is approached.
Advantages of Hydrothermal Reaction Conditions

Shorter, lower-temperature reactions compared with traditional solid-state method

Access to metastable phases

No problems with material loss due to volatility of starting materials

Better control of sample homogeneity and particle size

Possibility to include organic components that decompose at high temperatures

Applications in production of battery materials, nanostructured materials, catalysts, porous materials...
Equipment and General Procedure

H$_2$O, mineralizer

100-300 °C, hours or days
Reactions of Metal Oxides with Water

Basic oxides dissolve in acid:
\[ \text{BaO(s)} + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{OH}^-(aq) \]

Acidic oxides dissolve to produce acid:
\[ \text{SeO}_2(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{SeO}_3(aq) \quad \text{– a strong acid} \]
\[ \text{H}_2\text{SeO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HSeO}_3^-(aq) \]

Amphoteric oxides react with either acid or base:
\[ \text{Al}_2\text{O}_3(s) + 6 \text{H}_3\text{O}^+(aq) \rightleftharpoons 2 \text{Al}^{3+}(aq) + 9 \text{H}_2\text{O}(l) \]
\[ \text{Al}_2\text{O}_3(s) + 2 \text{OH}^-(aq) + 3 \text{H}_2\text{O}(l) \rightleftharpoons 2 [\text{Al(OH)}_4]^{-}(aq) \]
Many interesting oxides from our point of view are amphoteric!

For transition metals, oxide acidity increases with metal oxidation state:
\[ \text{MnO} < \text{MnO}_2 < \text{MnO}_3 \]
# Acid-Base Character of Oxides

<table>
<thead>
<tr>
<th>Basic Oxides</th>
<th>Acidic Oxides</th>
<th>Amphoteric Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_2\text{O} )</td>
<td>( \text{BeO} )</td>
<td>( \text{B}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>( \text{MgO} )</td>
<td>( \text{SiO}_2 )</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>( \text{CaO} )</td>
<td>( \text{GeO}_2 )</td>
</tr>
<tr>
<td>( \text{Rb}_2\text{O} )</td>
<td>( \text{SrO} )</td>
<td>( \text{As}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{O} )</td>
<td>( \text{BaO} )</td>
<td>( \text{Pb}_2\text{O}_3 )</td>
</tr>
</tbody>
</table>

- Basic oxides: \( \text{Li}_2\text{O} \), \( \text{BeO} \), \( \text{Na}_2\text{O} \), \( \text{K}_2\text{O} \), \( \text{Rb}_2\text{O} \), \( \text{Cs}_2\text{O} \)
- Acidic oxides: \( \text{B}_2\text{O}_3 \), \( \text{SiO}_2 \), \( \text{GeO}_2 \), \( \text{As}_2\text{O}_3 \), \( \text{Pb}_2\text{O}_3 \)
- Amphoteric oxides: \( \text{BeO} \), \( \text{SiO}_2 \), \( \text{GeO}_2 \), \( \text{As}_2\text{O}_3 \), \( \text{Pb}_2\text{O}_3 \)

*Note: The diagram illustrates the acid-base character of various oxides.*
Cation Hydrolysis in Water

\[ \text{M(H}_2\text{O)}_{x}^{n+} + \text{H}_2\text{O} \rightleftharpoons \text{M(H}_2\text{O)}_{x-1}(\text{OH})^{(n-1)+} + \text{H}_3\text{O}^+ \]

\[ \text{M(H}_2\text{O)}_{x-1}(\text{OH})^{(n-1)+} + \text{H}_2\text{O} \rightleftharpoons \text{M(H}_2\text{O)}_{x-2}(\text{OH})^{(n-2)+} + \text{H}_3\text{O}^+ \]

Further steps can lead to formation of hydroxides (e.g. Co(OH)$_2$, oxoanions (e.g. MnO$_4^{2-}$), and oxides (e.g. Fe$_3$O$_4$)

\[ \text{Fe(H}_2\text{O)}_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}_3\text{O}^+ \]

\[ \text{Fe(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}_4(\text{OH})_2^{+} + \text{H}_3\text{O}^+ \]

\[ \text{Fe(H}_2\text{O)}_4(\text{OH})_2^{+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}_3(\text{OH})_3 + \text{H}_3\text{O}^+ \]

And also

\[ 2 \text{Fe(H}_2\text{O)}_5(\text{OH})^{2+} \rightleftharpoons \text{Fe}_2(\text{H}_2\text{O)}_8(\text{OH})_2^{4+} + 2 \text{H}_2\text{O} \]
What Determines the Extent of Cation Hydrolysis?

Multiple hydrolysis steps with favorable equilibrium constants are found for metals with high charge, small radius and high electronegativity.

\[ \text{Acidity } \propto \frac{Z^2}{r} \]

Note that cations that have high acidity when added to water also form acidic oxides.

Ex) Ti\(^{4+}\), Si\(^{4+}\)

Reaction of TiCl\(_4\) with water vapor is used in skywriting.
Demonstration: Fe³⁺(aq) Acidity

Dissolving an Fe³⁺ salt in water produces an acidic solution.

The hexaaquo complex is colorless, while Fe(H₂O)₅(OH)²⁺ has visible absorption and is brownish yellow.

Figure from Baes, C.F.; Mesmer, R.E. The Hydrolysis of Cations; Wiley-Interscience: New York, 1976.
Pourbaix Diagrams

A visual representation of speciation of a metal as a function of pH and potential.

Dashed lines indicate theoretical and practical stability zones for water.

Vertical boundaries – represent $K_{sp}$ data that depend only on pH and not on potential

Ex) $\text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) \rightleftharpoons \text{Fe(OH)}_3(\text{s})$ $K_{sp} = 4 \times 10^{-38}$

Horizontal boundaries – represent simple redox reactions that depend only on potential

Ex) $\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$ $E^o = 0.771 \text{ V}$

Diagonal boundaries – represent reactions that involve both redox and acid-base chemistry

Ex) $\text{FeO}_4^{2-}(\text{aq}) + 3e^- + 8 \text{H}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ $E^o = 2.20 \text{ V}$

Use the Nernst equation to find the slope:

$$E = E^o - \frac{0.0592}{n} V \cdot \text{mol} e^- \cdot \log Q$$

$$E = 2.20V - \frac{0.0592}{3} V \cdot \log \left[ \frac{[\text{Fe}^{3+}]}{[\text{FeO}_4^{2-}] [\text{H}^+]^8} \right]$$

$$E = 2.20V - (0.157 \cdot pH)V$$
Multiple lines between predominance regions correspond to different total Fe concentrations.

Diagrams can differ in complexity (number of different species considered).

basic oxide/hydroxide

amphoteric oxide

Synthesis of Delafossite-Type Oxides, ABO$_2$

Edge-sharing BO$_6$ octahedra

A cations

All reactions carried out hydrothermally (180-210 °C) in concentrated NaOH solutions.

A = Ag$^+$, Cu$^+$ (oxides primarily defined as basic)
B = Sc$^{3+}$, Co$^{3+}$, Fe$^{3+}$, Y$^{3+}$, La$^{3+}$, Ga$^{3+}$, In$^{3+}$, Al$^{3+}$...

### Accounting for Success and Failure with Acid-Base Character

<table>
<thead>
<tr>
<th>A-cation source</th>
<th>B-cation source</th>
<th>[NaOH]</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂O</td>
<td>Al₂O₃</td>
<td>0.9</td>
<td>CuAlO₂</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>Al₂O₃</td>
<td>0.9</td>
<td>AgAlO₂</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>CoOOH</td>
<td>2.0</td>
<td>CuCoO₂, Co₃O₄</td>
</tr>
<tr>
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<td>AgCoO₂, Co₃O₄</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Sc₂O₃</td>
<td>2.5</td>
<td>CuScO₂, ScOOH</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>Sc₂O₃</td>
<td>2.5</td>
<td>AgScO₂</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>La₂O₃</td>
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<tr>
<td>Ag₂O</td>
<td>La₂O₃</td>
<td>2.5</td>
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</tbody>
</table>

### Rule of thumb: minimum solubility required for each reactant oxide is approximately $10^{-4}$ M
CuAlO$_2$ and AgAlO$_2$ both synthesized at 0.9 M NaOH – Al$_2$O$_3$ is the “classic” amphoteric oxide; has solubility on the order of $10^{-1}$ M at 200 °C, 0.5 M NaOH.

CoOOH has amphoteric character but requires a larger [NaOH] than Al$_2$O$_3$ in order to react.

Reactions with Sc$_2$O$_3$ illustrate difference in acidity between Cu$_2$O and Ag$_2$O; max. solubility for Ag$^+$ is $10^{-2.5}$ at 200 °C, compared with $10^{-4}$ for Cu$^+$.

Reactions with Y$_2$O$_3$, Eu$_2$O$_3$, and La$_2$O$_3$ returned insoluble hydroxides – these are insufficiently acidic to react in base.
Cookies frequently contain both baking soda (NaHCO$_3$) and baking powder (a mixture of NaHCO$_3$, CaHPO$_4$, and NaAl(SO$_4$)$_2$).

Baking soda requires an acid to react with the bicarbonate. Baking powder provides its own through hydrolysis of the aluminum cation and reaction of the hydrogen phosphate ion with water.
Example 2: Nb and Ta Pyrochlores

A$_2$B$_2$O$_6$O$	ext{'}$

A$_2$O$	ext{'}$

B$_2$O$_6$

network

viewed along [110]
Hydrothermal Synthesis

\[
\begin{align*}
M_2O_5(s) + 2 \text{KOH(aq)} & \xrightarrow{\text{KOH}, 250 \degree C, 3-5 \text{ days}} K_{2-x}M_2(O,OH)_6 \cdot nH_2O(s) + H_2O(l) \\
M & = \text{Nb, Ta}^* \\
x & = 0.74, n = 1.3 \text{ for Ta} \\
x & = 0.73, n = 1.2 \text{ for Nb}
\end{align*}
\]

Ion-Exchange Reactions

<table>
<thead>
<tr>
<th>Exchanged cation</th>
<th>Ionic radius (Å) (coord. # = 8)</th>
<th>Refined lattice parameter (Å)</th>
<th>Metal ratio (EDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺ (un-exchanged)</td>
<td>1.65</td>
<td>10.621</td>
<td>1.25 K: 2 Ta</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.32</td>
<td>10.533</td>
<td>0.89 Na: 2 Ta</td>
</tr>
</tbody>
</table>

**Graph:**
- **Legend:**
  - Na-exchanged
- **Axes:**
  - X-axis: CuKα 2θ (°)
  - Y-axis: counts
- **Graph Description:**
  - The graph shows the X-ray diffraction patterns for Na-exchanged samples, with peaks indicating the crystalline structure of the material.
  - The diffractogram displays typical sharp and broad peaks characteristic of crystalline materials.
  - The intensity of the peaks suggests a high degree of crystallinity.

**Table Summary:**
- The table provides a comparison of ionic radii, lattice parameters, and metal ratios for exchanged cations.
- The data indicates that Na⁺ has the smallest ionic radius compared to K⁺, affecting the lattice parameter and, consequently, the metal ratio extracted through EDS analysis.
Ion-Exchange Reactions

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<tbody>
<tr>
<td>K⁺ (un-exchanged)</td>
<td>1.65</td>
<td>10.653</td>
<td>1.14 K: 2 Nb</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>1.10</td>
<td>10.640</td>
<td>0.68 K: 0.30 Mn: 2 Nb</td>
</tr>
<tr>
<td>Sn²⁺</td>
<td>1.36</td>
<td>10.615</td>
<td>0.23 K: 0.16 Sn: 2 Nb</td>
</tr>
</tbody>
</table>
Hydrothermal Synthesis of Inorganic-Organic Hybrid Networks

Thousands of synthesized compounds can be described as coordination polymers, hybrid inorganic-organic networks, metal-organic frameworks...

Extensive linkages limit solubility under ambient conditions, and organic component requires mild reaction conditions.
Laboratory and field studies show that organic acid exposure is a major cause of corrosion in lead-tin alloy organ pipes.

Photos courtesy of Ibo Ortgies, Göteborg Organ Art Center
Basic lead formate:

\[ 2\text{PbO} + 2\text{HCOOH} \xrightarrow{\text{H}_2\text{O}} \text{Pb}_2\text{O(CHOO)}_2 \]

\[ \xrightarrow{120 \degree \text{C}} \xrightarrow{17 \text{ hrs}} \]

Basic lead acetate:

\[ \text{Pb(CH}_3\text{COO)}_2 \cdot 3\text{H}_2\text{O} + 2\text{PbO} \xrightarrow{\text{H}_2\text{O}} \text{Pb}_3\text{O}_2(\text{CH}_3\text{COO})_2 \cdot (0.5)\text{H}_2\text{O} \]

\[ \xrightarrow{120 \degree \text{C}} \xrightarrow{10 \text{ hrs}} \]

Pb$_4$O tetrahedron

Pb$_2$O$_2^{2+}$ chain

Pb$_3$O$_2^{2+}$ chain
Basic lead acetate:

Acetate ions link Pb$_3$O$_2$$^{2+}$ chains to form two-dimensional layers.
Basic lead formate:

Formate ions link $\text{Pb}_2\text{O}^{2+}$ chains into a three-dimensional network.
Analysis of Lead Coordination Environments

Basic lead acetate:

- BVS = 2.05
- BVS = 1.99

Basic lead formate:

- BVS = 1.94

Pb$^{2+}$: [Xe] 4f$^{14}$5d$^{10}$6s$^2$

Ideal bond valence sum (BVS) = 2
Non-Aqueous Systems: Growth of MOFs and ZIFs

MOF: Metal-Organic Framework

Synthesized from Co(CF$_3$SO$_3$)$_2$ and 1,4-benzenedi(4’pyrazoyl) in diethylformamide (DEF) at 130 °C. DEF decomposes to form amines that deprotonate the ligand.

Non-Aqueous Systems: Growth of MOFs and ZIFs

ZIF: Zeolitic Imidazolate Framework

Three-dimensional networks with tetrahedral topologies

Synthesized from hydrated metal salts, protonated imidazole ligands (HIm) and amide solvents at 85-150 °C

Non-Aqueous Systems: Chalcogenide Synthesis

Use of amine-based synthesis prevents unwanted metal hydrolysis, and amine can serve as a reactant as well as a solvent.

\[ S_8 \text{ ring can be activated by ring-opening nucleophilic attack by an amine – may also be true for other elemental chalcogenides.} \]

\[ \text{[In(}en\text{)}_3][\text{In}_5\text{Te}_9(\text{en})_2]\cdot0.5\text{en} \]

Synthesized from KIn₂, Te, and ethylenediamine (en) at 190 °C

Undergraduate Research in Materials Chemistry at Oberlin

Solvothermal Synthesis of Polymorphs of M(ethylenediamine)$_3$MoS$_4$ (M = Ni, Co, Mn)


Hydrothermal and Ion-Exchange Syntheses of Nb and Ta Defect Pyrochlores

Corrosion of Lead-Tin Alloy Organ Pipes and Crystal Chemistry of Basic Lead Carboxylates

Undergraduate Research in Materials Chemistry at Oberlin

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Michaela Hull, OC ’10
Joshua Greenfield, OC ’11
Katie Mauck, OC ‘09
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