Class 6.2
Acids and Bases

Friday, October 8
CHEM 462
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Table 8.3 From Jolly, “Modern Inorganic Chemistry” Aqueous pKa values of the binary hydrides of the nonmetals

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>NH₃</td>
<td>H₂O</td>
<td>HF</td>
</tr>
<tr>
<td>~ 44</td>
<td>39</td>
<td>15.74</td>
<td>3.15</td>
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<tr>
<td>SiH₄</td>
<td>PH₃</td>
<td>H₂S</td>
<td>HCl</td>
</tr>
<tr>
<td>~35</td>
<td>27</td>
<td>6.89</td>
<td>-6.3</td>
</tr>
<tr>
<td>GeH₄</td>
<td>AsH₃</td>
<td>H₂Se</td>
<td>HBr</td>
</tr>
<tr>
<td>25</td>
<td>≤23</td>
<td>3.7</td>
<td>-8.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂Te</td>
<td>Hl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6</td>
<td>-9.3</td>
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</tbody>
</table>

Acidic and Basic Oxides

- The oxides that one uses to form acids and bases in aqueous solution often have reactivity that reflects their acidic or basic character.
- Examples: Li₂O, CaO, and BaO react with water to form basic solutions and can react with acids directly to form salts. Likewise, SO₃, CO₂, and N₂O₅ form acidic aqueous solutions and can react directly with bases to give salts.
**Oxides as Acid and Basic Anhydrides**

**Basic Oxides** (usually “ionic”)

CaO + 2H₂O → Ca²⁺ + 2OH⁻,  
moderately strong base

[O²⁻] + H₂O → 2OH⁻  K > 10²²

Alkali metal and alkaline earth oxides are basic (dissolve in acid).

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**Acidic Oxides (Acid Anhydrides)**

Element-oxygen (E–O) bond not broken on dissolution

**either**

- an E – O – E group is hydrolyzed by water
- water is added across a double bond

Acidic Oxides not soluble in water will dissolve in basic aqueous solutions to produce salts

e.g. As₂O₃ + 2NaOH(aq) → 2NaH₂AsO₃

(Often seen for anhydrides of weaker acids.)

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**Examples**

(Diagram showing dissociation of various oxides into their respective ions.)
**Amphoteric Oxides**

Dissolve in acids or bases - if strong enough.
E.g., BeO, SnO, certain forms of Al₂O₃

In strong acids: \( \text{ZnO} + 2\text{HCl(aq)} \rightarrow \text{ZnCl₂(aq)} \)
\( \text{ZnO} + 2\text{HNO₃(aq)} \rightarrow \text{Zn(NO₃)₂}^2+ + \text{NO₃}^- \)

In strong base: \( \text{ZnO} + 2\text{NaOH(aq)} \rightarrow 2\text{Na}^+(aq) + [\text{Zn(OH₄)}^{2-}]^2- (aq) \)

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**Lux-Flood Concept (Oxide Solids)**

- **Acid:** Oxide ion acceptor
- **Base:** Oxide ion donor
  - A generalization that includes reactions between solids when water never gets involved. E.g.,
    \( \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \)
    \( 3\text{Na}_2\text{O} + \text{P}_2\text{O}_5 \rightarrow 2\text{Na}_3\text{PO}_4 \)
    \( \text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3 \)

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**Other Oxides**

Many oxides (particularly of the transition metals) are difficult to classify as acidic or basic because redox chemistry is more important.
E.g. \( \text{MnO}_2 + 4\text{H}^+ (aq. \text{conc.}) \rightarrow \text{Mn}^{2+}(aq) + \text{I}_2 + 2\text{H}_2\text{O} + 2\text{I}^- \)
Hydrolysis of Metal Complexes
can give acidic solutions

<table>
<thead>
<tr>
<th>Metal Complex</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
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</thead>
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<td>[Fe(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>2.46</td>
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<td>4.85</td>
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<td>5.89</td>
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<td>[Cu(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>7.49</td>
</tr>
<tr>
<td>[Ni(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;6&lt;/sub&gt;]&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>9.03</td>
</tr>
</tbody>
</table>

Examples of Acids From Solvolyzed Metals

**Aqua Acids** (solvolyis)  Al<sup>3+</sup> solutions are acidic

\[
\text{AlCl}_3(s) + H_2O \rightarrow \text{Al}^{3+}(aq) + \text{Cl}^-(aq)
\]

(w/sm. amts of water, HCl gas is evolved):

\[
\text{AlCl}_3 + H_2O \rightarrow \text{Al(OH)}_3 + 3\text{HCl}
\]

\[
\rightarrow \text{AlCl}_2(\text{OH})\cdot n\text{H}_2\text{O} \text{ complex}
\]

\[
\rightarrow \text{AlCl}(\text{OH})_2 + n\text{H}_2\text{O}
\]

Highly charged cations with small radii make for stronger acids:

[Fe(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup> fairly weak, [Fe(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> is much stronger. \( r(\text{Fe}^{3+}) < r(\text{Fe}^{2+}) \), the smaller, more highly charged (more polarizing) cation withdraws more e\(^{-}\) density from coordinated water.

More than size is involved:

\( r(\text{Al}^{3+}) < r(\text{Fe}^{3+}) \) ionic radii, but [Fe(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> is stronger than [Al(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>

Fe<sup>III</sup>–O bonding probably more covalent (smaller electronegativity diff. than Al/O).
Acid-Base behavior of Metal Ions not so simple…

Ions like $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ are often used as examples of cations that form acidic aqueous solutions, however acid-base equilibria for the “ions” are not simple.

[Compare: $\text{ClCH}_2\text{COOH}$ $\quad \text{pK}_a = 2.85$
— has a “normal” titration curve (pH vs. added base). What does it look like?]

An acidic $\text{[Al(OH}_2)_6]^{3+}$ solution will not titrate this way. Why?

$[\text{Al(OH}_2)_6]^{3+}$ is deprotonated, then…

e.g., $[\text{Al(OH}_2)_6]^{3+} + \text{CH}_3\text{COO}^- \rightleftharpoons [\text{Al(OH}_2)_5(\text{OH})]^2^+ + \text{CH}_3\text{COOH}$

condensation occurs:

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$

$\text{OH}^-$

$\text{Al(OH)}_3^-$

Transition Metals in High Ox. States: Acidic

Metals in very high oxidation states form strong, largely covalent, bonds with oxygen

$\rightarrow$ weakens O-H bonds!

e.g. $\text{CrO}_4^{2-}$ weak conjugate base of chromic acid

$+ \text{H}_2\text{O}^+ \rightarrow \text{[CrO}_4^{2-} \text{(OH)}]^{2-} \text{dichromate}$

e.g. $\text{MnO}_4^{-}$ very weak conjugate base of permanganic acid (both are powerful oxidants)
Lewis acids and Bases (orbital viewpoint)

(1) Metal cations (Lewis acids) & Ligands (Lewis bases)
(2) p-block Lewis Acids: Incomplete octets
e.g. B(CH₃)₃, AlCl₃

- Review of bonding
- Lewis acidity Trend for BX₃ (X = F, Cl, Br)?

AlCl₃: exists as Al₂Cl₆ in gas phase

Familiar application: Friedel-Crafts acylation
To be discussed later: Chloroaluminate based Ionic Liquids

Molecules with low-lying LUMOs

- E.g. (review CO₂ and SO₃ examples).
SO₂: can function as a Lewis acid or Lewis base:
- SO₂ as an acid (involvement of LUMO)
- SO₂ as a Lewis base - use of S-localized (HOMO) or O-localized lone-pairs
SO₃ is very electrophilic — strong Lewis acidity:

- electronic structure (review)
- Oleum: formed by adding SO₃ to H₂SO₄.