Lecture 9

Acids and Bases

Suggested reading: Chapter 4.2-4.11
Proton gain can be understood in terms of a thermodynamic cycle: if the proton gain enthalpy (or energy) is large and negative, corresponding to exothermic proton attachment, proton affinity is high → strongly basic material.

The stronger an acid, the weaker its conjugate base.

Bronsted theory: proton acceptors/donors

Acids and bases are measured by their $K$.

$pK = -\log K$

$pH = -\log [H_3O^+]$

If $K_{a,b} < 1$, weak acid/base.
Can we distinguish the strengths of these acids in water?

• Both will transfer their protons completely to give $\text{H}_3\text{O}^+$
• Water is said to have a leveling effect that brings all the stronger acids down to the acidity of $\text{H}_3\text{O}^+$. 
Solvent Levelling

• An acid that is weak in water may appear strong in a solvent that is a more effective proton acceptor.

• In sufficiently basic solvents (i.e., liquid ammonia), almost all acids seem strong.

\[
\text{HA(sol) + HSol(l)} \rightarrow \text{H}_2\text{Sol}^+(\text{sol}) + \text{A}^- (\text{sol})
\]

\[
K_a = \frac{[\text{H}_2\text{Sol}^+][\text{A}^-]}{[\text{HA}]}
\]

All acids with \(pK_a < 0\) (corresponding to \(K_a > 1\)) display the acidity of \(\text{H}_2\text{Sol}^+\) when they are dissolved in solvent HSol.

Example: HBr and HI have indistinguishable strengths in Water, even though HI is a stronger proton donor.
Solvent Levelling

• An acid that is weak in water may appear strong in a solvent that is a more effective proton acceptor.

• In sufficiently basic solvents (i.e., liquid ammonia), almost all acids seem strong.

\[
B(\text{sol}) + H\text{Sol}(l) \rightarrow BH^+(\text{sol}) + \text{Sol}^-(\text{sol})
\]

\[
K_b = \frac{[BH^+] [\text{Sol}^-]}{[B]}
\]

All bases with \(pK_b < 0\) (corresponding to \(K_b > 1\)) display the basicity of \(\text{Sol}^-\) when they are dissolved in solvent H\text{Sol}.

Example: Alkali metal amides (\(\text{NH}_2^-\)) or methides (\(\text{CH}_3^-\)) cannot be distinguished in water, since both anions generate OH\(^-\) and become fully protonated.
### Solvent Levelling

Which solvents could be used to differentiate the acidities of 
HCl (pKₐ=-6) and HBr (pKₐ=-9)?

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Effective pH in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorosulfuric acid, H₂SO₃F</td>
<td>-20</td>
</tr>
<tr>
<td>Hydrofluoric acid, HF</td>
<td>-10</td>
</tr>
<tr>
<td>Sulfuric acid, H₂SO₄</td>
<td>0</td>
</tr>
<tr>
<td>Methanoic acid, HCOOH</td>
<td>10</td>
</tr>
<tr>
<td>Ethanoic acid, CH₃COOH</td>
<td>20</td>
</tr>
<tr>
<td>Ethanol, CH₃CH₂OH</td>
<td>30</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>40</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td></td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td></td>
</tr>
</tbody>
</table>

*Acid-base discrimination window for a variety of solvents. The width is proportional to the autoprotolysis constant of the solvent.*
Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an “OH” group.

Three classes of –OH (hydroxy group) acids:

1. Aqua acids: the acid proton is on a water molecule coordinated to a central metal ion

\[
[Fe(OH_2)_6]^{3+} (aq) + H_2O(l) \rightarrow [Fe(OH_2)_5OH]^{2+} (aq) + H_3O^+ (aq)
\]

Hexaaquairon (III) ion
Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an “OH” group.

Three classes of \(-\text{OH} (\text{hydroxy group})\) acids:

2. Hydroxoacids: the acid proton is on a hydroxyl group without a neighboring oxo group (=O). For example, \(\text{Si} (\text{OH})_4\) and \(\text{Te}(\text{OH})_4\).

In the ocean, silicon exists primarily as orthosilicic acid. Algae polymerize this acid to form their cell walls.
Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an “OH” group.

Three classes of −OH (hydroxy group) acids:

3. Oxoacids: the acid proton is on a hydroxyl group with an oxo group (=O) attached to the same atom. For example, H$_2$SO$_4$.

*Sulfuric acid*
Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an “OH” group.
Three classes of –OH (hydroxy group) acids –
1) aqua acid,  2) hydroxoacid,  3) oxoacid.

The 3 classes can be regarded as successive stages in the deprotenation of an aqua acid:

\[ \ce{H2O - E - OH2 &<-> H+ \rightarrow HO - E - OH2^- &<-> H+ \rightarrow HO - E = O3^-} \]
Periodic Trends in Aqua Acid Strength

The strengths of aqua acids increase with increasing positive charge of the central metal ion and with decreasing ionic radius.

**Ionic model:** for s-block and early transition metals

\[
\xi = \frac{z^2}{(r + d)}
\]

- \( \xi \): Electrostatic parameter
- \( r \): Radius of ion
- \( d \): Diameter of water

![Diagram](image)
Periodic Trends in Aqua Acid Strength

The strengths of aqua acids increase with increasing positive charge of the central metal ion and with decreasing ionic radius.

**Covalent model:** for the later d-block and p-block metals

These metals repel the departing proton more strongly than is predicted from the ionic model → delocalized charge and covalent bonds between element and oxygen.
Periodic Trends in Aqua Acid Strength

The strengths of aqua acids increase with increasing positive charge of the central metal ion and with decreasing ionic radius.

Example: acidity sequence

\[ \text{Fe}(OH_2)_6^{2+} < \text{Fe}(OH_2)_6^{3+} < \text{Al}(OH_2)_6^{3+} \]

Large ionic radius and low charge

Smaller ionic radius and higher charge
Oxo Acids

**Mononuclear acids**: contain one atom of the parent element.

\[ \text{H}_2\text{CO}_3, \text{HNO}_3, \text{H}_3\text{PO}_4, \text{H}_2\text{SO}_4. \]

**Substituted oxoacids**:  
One of the hydroxyl groups can be replaced by another group.  
If replaced by a more electronegative group, acidity is increase.

Examples:  Fluorosulfuric acid \( \text{O}_2\text{SF(OH)} \)

\[ \rightarrow \text{F is very electronegative and draws electrons away from S...makes S seem more positive, therefore a stronger acid than O}_2\text{S(OH)}_2. \]

Aminosulfuric acid \( \text{O}_2\text{S(NH}_2\text{)OH}. \)
Pauling’s Rules

The strengths of a series of oxoacids containing a specific central atom with a variable number of oxo and hydroxyl groups are given by Pauling’s rules:

\[
p = \# \text{ oxo groups} \quad \quad \quad \quad \quad \quad \quad q = \# \text{hydroxyl groups}
\]

1. For the oxoacid \( O_p E(OH)_q \), \( pK_a = 8 - 5p \)

2. For the successive \( pK_a \) of polyprotic acids \((q>1)\), increase by 5 units for each successive proton transfer.

Example: identify the structures consistent with the following \( pK_a \)'s

\( \text{H}_3\text{PO}_4, : pK_a = 2.1 \)
Pauling’s Rules

The strengths of a series of oxoacids containing a specific central atom with a variable number of oxo and hydroxyl groups are given by Pauling’s rules:

\[ p = \# \text{ oxo groups} \quad \quad q = \# \text{hydroxyl groups} \]

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Example: identify the structures consistent with the following \( pK_a \)’s

\( H_3PO_3 \), \( pK_a = 1.8 \)
Polyoxo compound formation

Acids containing OH condense to form polyoxoanions

First class of Important Chemical reactions:
Condensation reactions

Two amino acids condensing to form a peptide bond (in red)

Note: precipitation usually occurs as the pH is increased
Orthophosphate condensation

$$2PO_4^- + 6H^+ \rightarrow HO-\overset{\cdot}{P}-O-\overset{\cdot}{P}-OH + H_2O$$

At pH=7.4, the P-O-P bond is unstable with respect to hydrolysis. In the presence of water, it will dissociate, releasing energy in the process

Releases 7.3 kcal/mol!
Orthophosphate condensation: Metabolism

ATP is in itself an unstable molecule which hydrolyzes to ADP and phosphate. This happens because the strength of the bonds between the phosphate residues in ATP is less than the strength of the bonds between its products, that is, ADP and phosphate with water. Normal cells maintain a certain ratio of ATP to ADP at a point ten orders of magnitude from equilibrium, with ATP concentrations more than a thousand times compared to ADP. Thus, displacement from equilibrium means that the hydrolysis of ATP in the cell releases a large amount of energy, which is in fact one of the most important functions of mitochondrial DNA.

Releases 7.3 kcal/mol!
Lewis Acid/Base Theory (1930’s)

A Lewis acid acts as an electron pair acceptor.
A Lewis base acts as an electron pair donor.

\[ A + :B \longrightarrow A-B \]

All the Bronsted acids are Lewis acids.
All the Bronsted bases are Lewis bases.
Lewis acidity is much broader than Bronsted acidity.
Examples of Lewis Acids

1) A metal cation can bond to an electron pair supplied by the base to form a coordination compound. $[\text{Co(OH}_2\text{)}_6]^{2+}$
   \[ \rightarrow \text{Will revisit in our discussion of complexes } \mathbb{C} \]

2) A molecule with an incomplete octet can complete its octet by accepting an electron pair.

![Lewis acid diagram](https://example.com/lewis_acid_diagram.png)
Examples of Lewis Acids

3) A molecule or ion with a complete octet may be able to arrange its valence electrons and accept an additional electron pair. \( \text{CO}_2 \) and \( \text{OH}^- \)

\[
\text{O} = \text{C} = \text{O} + \cdot \text{O-H} \rightarrow \text{O} = \text{C} \text{O}^- \cdot \text{OH}
\]

Lewis acid

4) A molecule or ion may be able to expand its valence shell (or simply be large enough) to accept another electron pair.
Example: \( \text{SF}_4 \) to \( \text{SF}_6^{2-} \)

Lewis acid
Classifications of Lewis Acids and Bases

Soft and hard acids and bases are identified empirically by the strengths to form complexes with halide ion bases (measured by equilibrium constant of formation)

Hard acids bond in the order:

\[ I^- < Br^- < Cl^- < F^- \]

\[ R_3P < R_3N, \]

or \[ R_2S < R_2O. \]

Hard acid and base: electrostatic interaction

Soft acid and base: large polarizability, covalent bonding.
Trends in stability constants

Rule of thumb:

- Small cations are hard and form complexes with small anions.

- Large cations (such as Hg) are more polarizable and are soft.
Elements & Solvents

**Hard:** Water, Alcohol, Ethers, Amines, DMSO: \((CH_3)_2SO\), DMF: \((CH_3)_2NCHO\), Acetonitrile: \(CH_3CN\), THF: Tetrahydrofuran

**Soft:** Thiol, Benzene

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### Table 4.5 The classification of Lewis acids and bases*

<table>
<thead>
<tr>
<th>Hard Acids</th>
<th>Hard Bases</th>
<th>Soft Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+), Li(^+), Na(^+), K(^+)</td>
<td>Fe(^{2+}), Co(^{2+}), Ni(^{2+})</td>
<td>Cu(^+), Au(^+), Ag(^+), Ti(^+), Hg(^{2+})</td>
</tr>
<tr>
<td>Be(^{2+}), Mg(^{2+}), Ca(^{2+})</td>
<td>Cu(^{2+}), Zn(^{2+}), Pb(^{2+})</td>
<td>Pd(^{2+}), Cd(^{2+}), Pt(^{2+}), Hg(^{2+})</td>
</tr>
<tr>
<td>Cr(^{2+}), Cr(^{3+}), Al(^{3+})</td>
<td>SO(_2), BBr(_3)</td>
<td>BH(_3)</td>
</tr>
<tr>
<td>SO(_3), BF(_3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Borderline Acids</th>
<th>Borderline Bases</th>
<th>Soft Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_2), SO(_3(^{2-}), Br(^-)</td>
<td>N(_3), N(_2)</td>
<td>H(^-), R(^-), SCN(^-), CO, I(^-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_4(^{2-}), PO(_3(^{2-}), ClO(_4(^{-})</td>
<td>C(_6)H(_5)N, SCN(^-)</td>
<td>R(_2)S</td>
</tr>
</tbody>
</table>

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**Important rules:**
- Hard acids tend to bind to hard bases
- Soft acids tend to bind to soft bases.

* The underlined element is the site of attachment to which the classification refers.
Consequences of Softness/Hardness

Cation Exchange in Nanoparticles

• The monovalent Ag⁺ cation is softer than the divalent Cd²⁺ cation. Therefore, MeOH, a hard base, preferentially binds Cd²⁺ cations. Similarly, the soft base, TBP, binds strongly to Ag⁺ cations.

Geochemistry: Mineral abundance

Goldschmidt classification:
• Li, Mg, Ti, Al Cr exist in oxide form, (Lithophile elements)
• Cd, Pb, Sb, Bi exist in chalcogenide form, (chalcopyrite elements).
Basic Reaction Chemistry