**Thermodynamics**

\[ HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq) \]

- For most weak acids, \(\Delta S^\circ\) is \(-88 \text{ J/mol}\cdot\text{K}\) (dominated by order imposed in solvating the proton)

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]

\(\Delta G^\circ\) increases with increasing T; acidity constant declines.

**Polyprotic Acids**

- In aqueous solution \(pK_{a2} \approx pK_{a1} + 5\), \(pK_{a3} \approx pK_{a2} + 5\) when both OH groups of an oxoacid are bound to the same atom. This rule is basically of electrostatic origin.

<table>
<thead>
<tr>
<th>Polyprotic Acids</th>
</tr>
</thead>
</table>
| \begin{tabular}{|l|l|l|}
| HA & A^- & pK_a \hline
| H_3PO_4 & H_2PO_4^- & 2.12 \hline
| H_2PO_4^- & HPO_4^{2-} & 7.2 \hline
| HPO_4^{2-} & PO_4^{3-} & 12.7 \hline
| H_2SO_4 & HSO_4^- & \text{-2*} \hline
| HSO_4^- & SO_4^{2-} & 1.9 \hline
| H_2CO_3 & HCO_3^- & 3.8^\dagger \hline
| HCO_3^- & CO_3^{2-} & 10.3^\dagger \hline
\end{tabular} |
**Oxo Acids**

**Systematics (Pauling’s Rules)**

- For oxoacids $\text{O}_p\text{E(OH)}_q$: $\text{pK}_a \approx 8 - 5p$ (same rule, but includes a reference $\text{pK}_a$)
- The more oxygen atoms there are to delocalize charge in the conjugate base, the stronger the acid.
- This expression indicates that -OH groups don’t have much effect in delocalizing charge, e.g., (see next slide)

Some of the apparent exceptions

1. $\text{H}_3\text{PO}_3$ and $\text{H}_5\text{AsO}_3$ would be expected to have similar acidities, but structural differences are crucial!
2. The value of $\text{H}_2\text{CO}_3$ has been adjusted to reflect the fact that this species exists only to a slight extent in $\text{H}_2\text{O}$:
   
   $$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad \text{K}_{eq} = 2 \times 10^{-4}$$

   similarly, “sulfurous acid” not significant species

   $$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3 \quad \text{K}_{eq} < 10^{-4}$$

Pauling’s Rules for $\text{O}_p\text{E(OH)}_q$ acids:

1. $\text{pK}_a = 8 - 5p$
2. If $q > 1$, then successive $\text{pK}_a$ values should increase by about 5
Trends for dicarboxylic acids

<table>
<thead>
<tr>
<th></th>
<th>pK_{a1}</th>
<th>pK_{a2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic</td>
<td>1.23</td>
<td>4.28</td>
</tr>
<tr>
<td>malonic</td>
<td>2.85</td>
<td>5.70</td>
</tr>
<tr>
<td>succinic</td>
<td>4.19</td>
<td>5.48</td>
</tr>
<tr>
<td>adipic</td>
<td>4.42</td>
<td>5.41</td>
</tr>
</tbody>
</table>

As the positions of deprotonation get further apart, the influence that the two sites exert on each other declines.

Origin of the Trend for HX Acid Strengths

For HF, HCl, HBr, HI

\[ \Delta G^\circ \text{ (kJ/mol)} \]

- HX(aq) \rightarrow HX(g) \quad 24, -4, -4, -4
- HX(g) \rightarrow H^+(g) + X^-(g) \quad 535, 405, 339, 272
- H^+(g) + X^-(g) \rightarrow H^+(aq) + X^-(aq) \quad 973, 953, 975, 1005
- HX(aq) \rightarrow H^+(aq) + X^-(aq) \quad 18, -40, -54, -57

\[ pK_a = -\log K_a = \frac{\Delta G^\circ}{2.303RT} = \frac{+\Delta G^\circ}{5.706} \text{ (kJ/mol at } T = 298K) \]

Solvent Leveling

The products of solvent autoprotolysis determine the strongest acid-base pairs possible in a protic solvent.

Thus, in water:
- No acid stronger than H_3O^+ is possible
- No base stronger than OH^- is possible
**Solvent Leveling**

Example, HCl, HBr, and HI are considered to form a series with acid strength, but this doesn’t refer to pH measurements carried out in H₂O!

In acetic acid:

\[
\begin{align*}
  &X^- + \text{CH}_3\text{COOH} \\
  \xrightarrow{\text{equivalent}} \\
  &X^- + \text{CH}_3\text{COO}^-
\end{align*}
\]

\[K_a(\text{HI}) > K_a(\text{HBr}) > K_a(\text{HCl})\]

**Solvent leveling for bases is analogous:**

\[
\begin{align*}
  &\text{KOH} + \text{H}_2\text{O}(l) \rightarrow \text{K}^+(aq) + \text{OH}^-(aq) \\
  &\text{KOR} \quad \text{K}^+(aq) + \text{OH}^-(aq) + \text{ROH} \\
  &\text{KNH}_2 \quad \text{K}^+(aq) + \text{OH}^-(aq) + \text{NH}_3 \\
  &\text{LiCH}_3 \quad \text{Li}^+(aq) + \text{OH}^-(aq) + \text{CH}_4
\end{align*}
\]

**Autoprotolysis constants determine the ranges of acid and base strengths:**

Examples:

\[
\begin{align*}
  &2\text{NH}_3(l) \rightarrow \text{NH}_4^+(am) + \text{NH}_2^-(am) \\
  &\text{pK}_{am} \approx 33 \quad (\text{pK}_w = 14)
\end{align*}
\]

DMSO: \[\text{pK}_{\text{DMSO}} = 37\]
In DMSO, much stronger bases can be studied:

\[
\begin{align*}
\text{KPH}_2(s) + \text{H}_2\text{O} & \quad \rightarrow \quad \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{PH}_3(\text{aq}) \\
\text{KPH}_2(s) + \text{DMSO} & \quad \rightarrow \quad \text{K}^+(\text{solv}) + \text{PH}_2^-\text{(solv)} + \text{DMSO}
\end{align*}
\]

Note: Care must be exercised in comparing acidities! Solvation of conjugate acid-base pairs differs from solvent to solvent.

“pH” ranges in Selected Solvents

Importance of solvation:

Examples:

\[
\begin{align*}
2\text{H}_2\text{O}(g) & \quad \rightarrow \quad \text{H}_3\text{O}^+(g) + \text{OH}^-(g) \\
\Delta H &= +1586 \text{ kJ/mol}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3(g) & \quad \rightarrow \quad \text{CH}_2^-(g) + \text{H}^+(g) \\
\Delta H &= +1635 \text{ kJ/mol}
\end{align*}
\]

Both large and positive, but stabilization by solvation makes the first process significant in water.