### Thermodynamics of Complex Formation

Thermodynamic trends related to Crystal (or Ligand) Field Stabilization Energy (CFSE):

<table>
<thead>
<tr>
<th>$d''$</th>
<th>Oh configuration</th>
<th>CFSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$t_{2g}^1 e_g^0$</td>
<td>-0.4 $\Delta_{\text{oct}}$</td>
</tr>
<tr>
<td>2</td>
<td>$t_{2g}^2 e_g^0$</td>
<td>-0.8</td>
</tr>
<tr>
<td>3</td>
<td>$t_{2g}^3 e_g^0$</td>
<td>-1.2</td>
</tr>
<tr>
<td>4</td>
<td>$t_{2g}^3 e_g^1$</td>
<td>-0.6</td>
</tr>
<tr>
<td>5</td>
<td>$t_{2g}^3 e_g^2$</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>$t_{2g}^4 e_g^2$</td>
<td>-0.4</td>
</tr>
<tr>
<td>7</td>
<td>$t_{2g}^5 e_g^2$</td>
<td>-0.8</td>
</tr>
<tr>
<td>8</td>
<td>$t_{2g}^6 e_g^2$</td>
<td>-1.2</td>
</tr>
<tr>
<td>9</td>
<td>$t_{2g}^6 e_g^3$</td>
<td>-0.6</td>
</tr>
<tr>
<td>10</td>
<td>$t_{2g}^6 e_g^4$</td>
<td>0</td>
</tr>
</tbody>
</table>

(See Section 21.10 of H&S for discussion of these ideas)

- both lattice energies and hydration energies show the classic ‘double-humped’ pattern predicted by the CFSE
- also correctly predicts that there will be no thermodynamic energy preference for Td vs. Oh based on CFSE at $d^0$, $d^5$ (high spin) or $d^{10}$ electronic configurations
- strongest thermodynamic preference for Oh over Td will be at $d^3$ and $d^8$ ions
Note: general increase in both hydration enthalpy and lattice energy as ion size decreases due to $Z_{\text{eff}}$ effects
**Equilibrium constants and complex formation** (see H&S 7.11-7.13)

Some basic questions we would like answers to:

- *how strong is the metal ligand binding?*
- *what happens when we add a ligand to an aqueous solution of a metal ion?*
- *how is ligand binding related to specific properties of the ligand and the metal?*

Consider the reaction between a hexa(aqua) metal $2^+$ ion and another ligand $L$ in water:

\[
{\{M(H_2O)\}_6}^{2+} + L \rightleftharpoons {\{M(H_2O)_5(L)\}}^{2+} + H_2O
\]

\[
K = [{\{M(H_2O)_5(L)\}}^{2+}] [H_2O] / [{\{M(H_2O)_6\}}^{2+}][L]
\]

but since $[H_2O]$ is a constant in water, this can be incorporated into the equilibrium constant:

\[
K_1 = [{\{M(H_2O)_5(L)\}}^{2+}] / [{\{M(H_2O)_6\}}^{2+}][L]
\]

and we can do this for each subsequent step:

\[
{\{M(H_2O)_5(L)\}}^{2+} + L \rightleftharpoons {\{M(H_2O)_4(L)_2\}}^{2+} + H_2O
\]

\[
K_2 = [{\{M(H_2O)_4(L)_2\}}^{2+}] / [{\{M(H_2O)_5(L)\}}^{2+}][L]
\]
K is called a ‘stability constant’ (also known as a ‘formation constant’ or ‘binding constant’) and it is defined stepwise for each sequential replacement of water by L:

\[ K_1, K_2, K_3, K_4, K_5 \text{ and } K_6 \]

It is also possible to define an overall stability constant \( \beta \) for the complete substitution sequence:

\[ \{M(H_2O)_6\}^{2+} + 6L \leftrightharpoons \{M(L)_6\}^{2+} + 6H_2O \]

\[ \beta_6 = \frac{[\{M(L)_6\}^{2+}]}{[\{M(H_2O)_6\}^{2+}][L]^6} \]

and \( \beta_6 = K_1K_2K_3K_4K_5K_6 \)

OR \( \log \beta_6 = \log K_1 + \log K_2 + \log K_3 + \log K_4 + \log K_5 + \log K_6 \)

<table>
<thead>
<tr>
<th>M</th>
<th>L</th>
<th>\log K_1</th>
<th>\log K_2</th>
<th>\log K_3</th>
<th>\log K_4</th>
<th>\log K_5</th>
<th>\log K_6</th>
<th>\log \beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu^{2+}</td>
<td>NH₃</td>
<td>4.17</td>
<td>3.53</td>
<td>2.88</td>
<td>2.05</td>
<td></td>
<td></td>
<td>12.6</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>NH₃</td>
<td>2.80</td>
<td>2.24</td>
<td>1.73</td>
<td>1.19</td>
<td>0.75</td>
<td>0.03</td>
<td>8.7</td>
</tr>
<tr>
<td>Hg^{2+}</td>
<td>CN⁻</td>
<td>18.00</td>
<td>16.70</td>
<td>3.83</td>
<td>2.98</td>
<td></td>
<td></td>
<td>41.5</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>en</td>
<td>10.55</td>
<td>9.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.6</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>en</td>
<td>7.45</td>
<td>6.23</td>
<td>4.34</td>
<td></td>
<td></td>
<td></td>
<td>18.0</td>
</tr>
</tbody>
</table>
**K generally decreases with each subsequent added L**

- statistical effect (more likely to displace one of six water than say one of three)
- changes in ligand binding caused by entering ligand effects
- decreasing charge on metal when the incoming ligand is negatively charged
- steric crowding effects

**Determination of $K_n$ and $\beta$**

In principle, any technique that allows determination of the concentrations of $[M(L)_n(H_2O)_{6-n}]$ can be used BUT it can be shown that you need $n+2$ independent concentrations to determine $n$ stability constants $K$...assuming you know the starting concentrations $[M(H_2O)_6]$ and $L$, you need $n$ more measurements.

Most common techniques:

- **UV-Vis spectroscopy**
- **redox potentials by electrochemistry**
- **pH titrations**