The crystal field stabilization energy (CFSE) is an important factor in the stability of transition metal complexes. Complexes with high CFSE tend to be thermodynamically stable (i.e., they have high values of $K_a$, the equilibrium constant for metal-ligand association) and are also kinetically stable. They are kinetically stable because ligand substitution requires that they dissociate (lose a ligand), associate (gain a ligand), or interchange (gain and lose ligands at the same time) in the transition state. These distortions in coordination geometry lead to a large activation energy if the CFSE is large, even if the product of the ligand exchange reaction is also a stable complex. For this reason, complexes of Pt$^{4+}$, Ir$^{3+}$ (both low spin 5d$^6$), and Pt$^{2+}$ (square planar 5d$^8$) have very slow ligand exchange rates.

There are two other important factors that contribute to complex stability:

- **Hard-soft interactions** of metals and ligands (which relate to the energy of complex formation)
- The **chelate effect**, which is an entropic contributor to complex stability.

### Hard-soft interactions

**Hard acids** are typically small, high charge density cations that are weakly polarizable such as H$^+$, Li$^+$, Na$^+$, Be$^{2+}$, Mg$^{2+}$, Al$^{3+}$, Ti$^{4+}$, and Cr$^{6+}$. *Electropositive metals* in *high oxidation states* are typically hard acids. These elements are predominantly found in oxide minerals, because O$^{2-}$ is a hard base.

Some **hard bases** include H$_2$O, OH$^-$, O$^{2-}$, F$^-$, NO$_3^-$, Cl$^-$, and NH$_3$.

The hard acid-base interaction is primarily **electrostatic**. Complexes of hard acids with hard bases are stable because of the electrostatic component of the CFSE.

**Soft acids** are large, polarizable, electronegative metal ions in *low oxidation states* such as Ni$^0$, Hg$^{2+}$, Cd$^{2+}$, Cu$^+$, Ag$^+$, and Au$^+$. **Soft bases** are anions/neutral bases such as H$^-$, C$_2$H$_4$, CO, PR$_3$, R$_2$S, and CN$^-$. Soft acids typically occur in nature as sulfide or arsenide minerals.

The bonding between soft acids and soft bases is predominantly **covalent**. For example, metal carbonyls bind through a covalent interaction between a zero- or low-valent metal and neutral CO to form Ni(CO)$_4$, Fe(CO)$_5$, Co(CO)$_4^-$, Mn$_2$(CO)$_{10}$, W(CO)$_6$, and related compounds.

The preference for hard-hard and soft-soft interactions ("like binds like") is nicely illustrated in the properties of the copper halides:

<table>
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<tr>
<th></th>
<th>CuF</th>
<th>Cul</th>
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<tbody>
<tr>
<td></td>
<td>unstable</td>
<td>stable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CuF$_2$</th>
<th>Cul$_2$</th>
</tr>
</thead>
</table>

The compounds CuF and CuI₂ have never been isolated, and are thermodynamically unstable to disproportionation:

\[2\text{CuF(s)} \rightarrow \text{Cu(s)} + \text{CuF}_2(s)\]

\[2\text{CuI}_2(s) \rightarrow 2\text{CuI(s)} + \text{I}_2(s)\]

We will learn more about quantifying the energetics of these compounds in Chapter 9.

Contributors

- Adapted from the Wikibook constructed by Chemistry 310 students at Penn State University.