Copper Chemistry

Cu : \(1s^22s^22p^63s^23p^63d^{10}4s^1\)

- Cu has a **single s electron in its fourth shell**. One may be inclined to think, based on its electronic configuration, that it has similar properties to the alkali metals, in particular K, however this is not the case.

- The filled **d shell** is much **less effective** than a filled *p* shell at **shielding the s electron** from the nuclear charge (29 protons), such that the first ionization energy of Cu is higher than that of its closest alkali relative K (19 protons).

\[
\begin{align*}
\text{K} & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 4s^1 \\
& \quad \downarrow 4.34 \text{ eV} \\
\text{K}^+ & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \\
& \quad \downarrow 31.63 \text{ eV} \\
\text{K}^{2+} & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^5 \\
\text{Cu} & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 3d^{10} \, 4s^1 \\
& \quad \downarrow 7.73 \text{ eV} \\
\text{Cu}^+ & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 3d^{10} \\
& \quad \downarrow 20.29 \text{ eV} \\
\text{Cu}^{2+} & : 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 3d^9 \\
\end{align*}
\]

*Ionization energies (eV)*
• In contrast, the second (and third) ionization energy of Cu is much lower than that of K. This is as a result of the **diffuse nature of the d orbitals** which are **less penetrating** than the p orbitals surrounding the nucleus.

• It is these d electrons which give Cu its transition metal character with the existence of highly **colored paramagnetic Cu(II) complexes having d⁹ valence band configuration**.

• The d shell electrons impart **noble** character to Cu complexes resulting in **covalent character** justifying its Group 11 position in the periodic table relative to the highly **ionic** group 1 alkali metals. As a result solid state Cu systems display higher lattice energies than the alkali metals, even considering its smaller atomic radius:

\[
\begin{array}{c|c}
\text{Na}^+ & 0.95 \text{ Å} \\
\text{K}^+ & 1.33 \text{ Å} \\
\text{Cu}^+ & 0.93 \text{ Å}
\end{array}
\]

• The high covalency of elemental Cu, as a result of its interatomic **d--d bonding**, contributes to its **high thermal and electrical conductivity** (only second to Ag).
Cu(II)

- Cu(II) is the more stable state of copper
- Configuration $3d^9$ with one unpaired electron (paramagnetic)
- Incomplete $3d$ subshell permits $d$-$d$ state-to-state electronic transitions, which causes color (typically blue or green)

VS.

Cu(I)

- Cu(I) is an unstable state of copper
- Configuration $3d^{10}$ with no unpaired electrons (diamagnetic)
- Complete $3d$ subshell precludes $d$-$d$ state-to-state transitions, so Cu(I) is colorless like isoelectronic Zn(II), unless they are paired with a paramagnetic anion.
Cu(II)

- Most copper(II) compounds exhibit distortions from idealized octahedral geometry due to the Jahn-Teller effect.

- In CuCl$_2$(H$_2$O)$_2$ the copper can be described as a highly distorted $O_h$ complex, the Cu(II) center being surrounded by two water ligands and four chloride ligands, which bridge asymmetrically to other Cu centers.

- Copper(II) chloride dissociates in aqueous solution to give the blue color of [Cu(H$_2$O)$_6$]$^{2+}$ and yellow or red color of the halide complexes of the formula [CuCl$_{2+x}$]$^{x-}$. Concentrated solutions of CuCl$_2$ appear green because of the combination of these various chromophores.
Copper(II) chloride also forms a rich variety of other coordination complexes with ligands such as pyridine or triphenylphosphine oxide:

\[
\text{CuCl}_2 + 2 \text{C}_5\text{H}_5\text{N} \rightarrow [\text{CuCl}_2(\text{C}_5\text{H}_5\text{N})_2] \quad (\text{tetragonal})
\]

\[
\text{CuCl}_2 + 2 (\text{C}_6\text{H}_5)_3\text{P}=\text{O} \rightarrow [\text{CuCl}_2((\text{C}_6\text{H}_5)_3\text{P}=\text{O})_2] \quad (\text{tetrahedral})
\]

However "soft" ligands such as phosphines (e.g., triphenylphosphine), iodide, and cyanide as well as some tertiary amines cause reduction to give copper(I) complexes.

To convert copper(II) chloride to copper(I) derivatives it is generally more convenient to reduce an aqueous solution with the reducing agent sulfur dioxide:

\[
2 \text{CuCl}_2(\text{aq}) + \text{SO}_2 \rightarrow 2 \text{CuCl}(\text{s}) + 2 \text{HCl}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq})
\]
Cu(I)

- Although CuCl is insoluble in water, it **dissolves in aqueous solutions containing suitable donor molecules**.
- It forms complexes with halide ions, for example forming $\text{H}_3\text{O}^+ \text{CuCl}_2^-$ with concentrated hydrochloric acid. It also dissolves in solutions containing $\text{CN}^-$, $\text{S}_2\text{O}_3^{2-}$, and $\text{NH}_3$ to give complexes.

- Although only poorly soluble in water, its **aqueous solution are unstable with respect to disproportionation into Cu and CuCl}_2$. In part for this reason samples in air assume a green coloration.
Oxidation of Cu(I)

• In aqueous solution, \textit{Cu(I) is readily oxidized to Cu(II) in the presence of oxygen}:

\[
\begin{align*}
4(\text{Cu}^+ & \rightarrow \text{Cu}^{2+} + e^-) \hspace{2cm} E^\circ_{\text{Ox}} = -0.153 \text{ V} \\
\text{O}_2 + 4\text{H}^+ + 4 \text{e}^- & \rightarrow 2\text{H}_2\text{O} \hspace{2cm} E^\circ_{\text{Red}} = +1.229 \text{ V} \\
4\text{Cu}^+ + \text{O}_2 + 4\text{H}^+ & \rightarrow 4\text{Cu}^{2+} + 2\text{H}_2\text{O} \hspace{2cm} E^\circ_{\text{cell}} = 1.076 \text{ V}
\end{align*}
\]

• Moreover, \textit{Cu(I) undergoes spontaneous disproportionation} (autoredox):

\[
\begin{align*}
4(\text{Cu}^+ & \rightarrow \text{Cu}^{2+} + e^-) \hspace{2cm} E^\circ_{\text{Ox}} = -0.153 \text{ V} \\
\text{Cu}^+ + \text{e}^- & \rightarrow \text{Cu} \hspace{2cm} E^\circ_{\text{Red}} = +0.521 \text{ V} \\
2\text{Cu}^+ & \rightarrow \text{Cu} + \text{Cu}^{2+} \hspace{2cm} E^\circ_{\text{cell}} = +0.368 \text{ V}
\end{align*}
\]

• Thus $\Delta G$ is negative (spontaneous) for disproportionation.
Stabilizing Cu(I) in Compounds

- Simple Cu(I) compounds that can exist in the presence of water are those with *low-charge anions whose compounds are insoluble in water*:
  - CuCl, CuBr, CuI, and CuCN,

- In the solid, *stability depends on* the neighboring anion and the resulting *lattice energy* of the ionic solid.

- Copper(I) chloride is made by boiling a solution of HCl(*aq*) and CuCl₂(*aq*) in the presence of excess Cu.

- *Synthesis takes advantage of the stability of solid CuCl*, which makes redox between Cu and Cu²⁺ spontaneous:

\[
\text{Cu}(s) + \text{Cu}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow 2 \text{CuCl}(s) \quad E^\circ_{\text{cell}} = +0.442 \text{ V}
\]
\[ 
\text{Cu(s)} + \text{Cu}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2 \text{CuCl(s)} \\
E^\circ_{\text{cell}} = +0.442 \text{ V} 
\]

- In concentrated HCl solution, the dichlorocuprate ion, \([\text{CuCl}_2]^-\), is the actual product:

\[ 
\text{Cu(s)} + \text{Cu}^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons 2 [\text{CuCl}_2]^- (\text{aq}) 
\]

- On dilution with water, copper(I) chloride precipitates:

\[ 
[\text{CuCl}_2]^-(\text{aq}) \rightleftharpoons \text{CuCl(s)} + \text{Cl}^-(\text{aq}) 
\]

- Conversely, if CuCl(s) is added to a chloride solution, it will dissolve due to the driving force of forming the \([\text{CuCl}_2]^- (\text{aq})\) complex.
• The equilibrium can be displaced in either direction:

\[ 2 \text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{2+} \]

Anions or bridging ligands that form complexes with Cu\(^+\) may stabilize Cu\(^+\) so long as they do not form more stable complexes with Cu\(^{2+}\).

• In the synthesis, formation of \([\text{CuCl}_2]^-\)(aq) effectively removes Cu\(^+\) from the solution and drives the equilibrium to the left (LeChatelier’s Principle).

• By contrast, when CuCl(s) is treated with ethylenediamine Cu\(^+\) is oxidized to Cu\(^{2+}\) because the bis-ethylenediamine copper(II) complex is more stable than the copper(I) complex:

\[ 2 \text{CuCl}(s) + 2 \text{en} \rightleftharpoons [\text{Cuen}_2]^{2+}(aq) + \text{Cu}(s) + 2 \text{Cl}^-(aq) \]

• The copper(II) complex is favored by the chelating nature of en. With non-chelating ligands such as NH\(_3\) and pentamethylenediamine [H\(_2\)N-(CH\(_2\))\(_5\)-NH\(_2\)] the copper(I) complex is favored:

\[ [\text{Cu(NH}_3)_4]^{2+}(aq) + \text{Cu}(s) \rightleftharpoons 2 [\text{Cu(NH}_3)_2]^+(aq) \]
Copper(I) Iodide

- **Anions or bridging ligands** that form complexes with Cu\(^+\) **may stabilize** Cu\(^+\) so long as they do not form more stable complexes with Cu\(^{2+}\).

- **Copper(I) iodide precipitates when any Cu(II) salt is added to a KI(aq) solution.**

\[
2\text{Cu}^{2+}(aq) + 4\text{I}^-(aq) \rightarrow 2\text{CuI(s) + I}_2
\]

- \(\text{I}^-(aq)\) is a strong enough reducing agent to reduce Cu\(^{2+}(aq)\) to CuI(s):

\[
2\text{I}^- \rightarrow \text{I}_2 + 2e^- \quad E^\circ_{\text{Ox}} = -0.54 \text{ V}
\]

\[
2(\text{Cu}^{2+} + \text{I}^- + e^- \rightarrow \text{CuI})
\]

\[
2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2 \quad E^\circ_{\text{Red}} = +0.88 \text{ V}
\]

\[
E^\circ_{\text{cell}} = +0.34 \text{ V}
\]

- Here \(\text{I}^-(aq)\) is able to reduce Cu\(^{2+}(aq)\) to CuI(s).

\[
2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2
\]