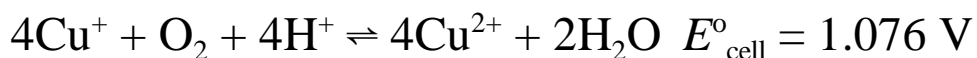
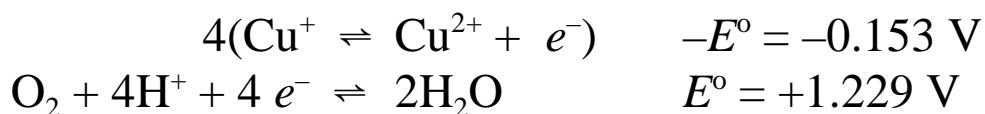


Cu(II) vs. Cu(I)

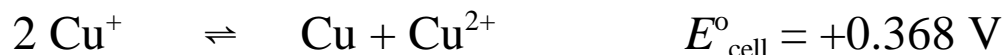
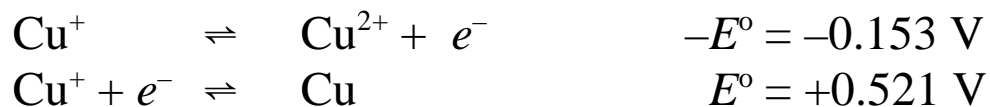
- Cu(II) is the stable state of copper.
 - ★ Configuration $3d^9$ with one unpaired electron makes Cu(II) compounds paramagnetic.
 - ★ Incomplete $3d$ subshell permits $d-d$ state-to-state electronic transitions, which causes color (typically blue or green).
- Cu(I) is an unstable state of copper.
 - ★ Configuration $3d^{10}$ with no unpaired electrons makes Cu(I) diamagnetic.
 - ★ Complete $3d$ subshell precludes $d-d$ state-to-state transitions, so Cu(I) is colorless like isoelectronic Zn(II).
 - Cu(I) compounds may be colored with certain anions
 - CuI(*s*) — pale yellow
 - Cu₂O(*s*) — brick red
 - ★ Fehling's solution, an alkaline solution of Cu²⁺ with sodium tartrate, reacts with reducing sugars such as glucose to give brick red Cu₂O.

Oxidation of Cu(I)

- In aqueous solution, Cu(I) is readily oxidized to Cu(II) in the presence of oxygen:



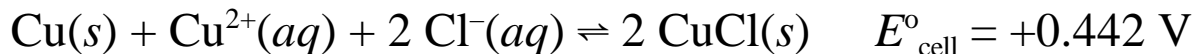
- Cu(I) undergoes spontaneous disproportionation (autoredox):



- ★ Thus ΔG 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, such CuCl, CuBr, CuI, and CuCN, whose compounds are *insoluble* in water.
- 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 Cu⁰ and Cu²⁺ spontaneous:

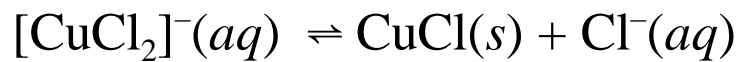


Stabilizing Cu(I) in Aqueous Chloride Solution

- In aqueous solution only small concentrations of Cu(I) can exist, $[\text{Cu}^+] < 10^{-2} \text{ M}$.
- Relative stability of Cu(I) in aqueous solution is strongly dependant on the nature of the anion or the presence of complexing ligands.
- In concentrated HCl solution, the initial product is the dichlorocuprate ion, $[\text{CuCl}_2]^-$, in solution:



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

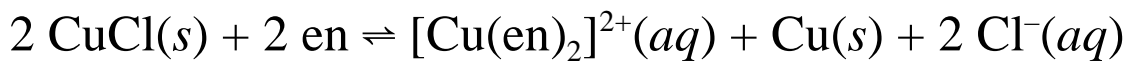


- Dilution reduces $[\text{Cl}^-]$, which drives the equilibrium to the right.
- Conversely, if $\text{CuCl}(s)$ is added to a chloride solution, it will dissolve due to the driving force of forming the $[\text{CuCl}_2]^-(aq)$ complex.

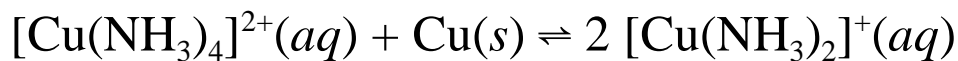
Stability of Cu^+ vs. Cu^{2+} Complexes

☞ Position of the $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}^0$ equilibrium in the presence of complexing ligands depends on the relative stability of the Cu^+ complex relative to the Cu^{2+} complex.

- 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, thereby driving the equilibrium to the left (LeChatelier's Principle).
- When $\text{CuCl}(s)$ is treated with the chelating ligand ethylenediamine Cu^+ is oxidized to Cu^{2+} , because the bis-ethylenediamine copper(II) complex is more stable than the copper(I) complex:



- With non-chelating ligands such as NH_3 and pentamethylenediamine $[\text{H}_2\text{N}-(\text{CH}_2)_5-\text{NH}_2]$ the copper(I) complex is favored.

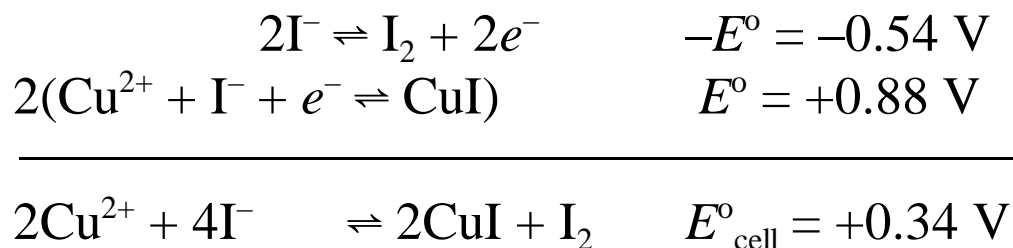


Copper(I) Iodide

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



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



Cu⁺ in Acetonitrile

- CuCl is soluble in acetonitrile, CH₃CN.
- ★ Cu(I) is effectively solvated by CH₃CN.
- ★ Cu(I) is actually more stable than Cu(II) in acetonitrile.
- ★ Tetrahedral ion [Cu(CH₃CN)₄]⁺ can be isolated in salts with large anions such as ClO₄⁻ and PF₆⁻.