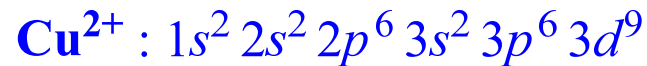
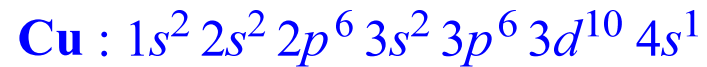
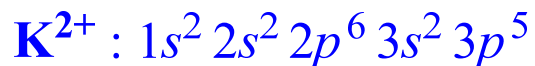
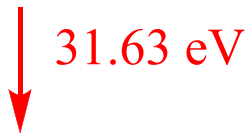
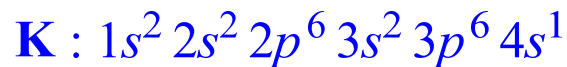


Copper Chemistry



- 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*).



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 d^9 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:

Na ⁺	0.95 Å
K ⁺	1.33 Å
Cu ⁺	0.93 Å

- 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**)

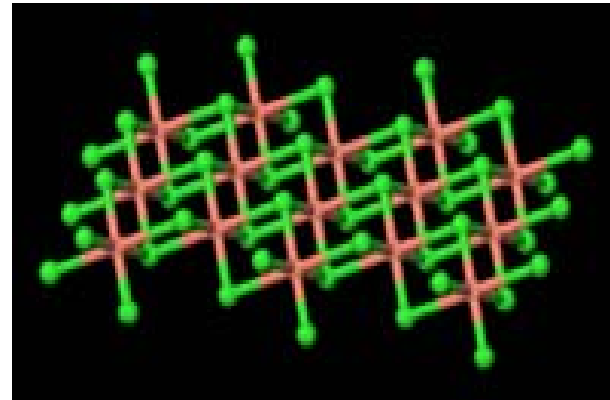
vs.

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 $\text{CuCl}_2(\text{H}_2\text{O})_2$ 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 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and yellow or red color of the halide complexes of the formula $[\text{CuCl}_{2+x}]^{x-}$. 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:



- 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:**



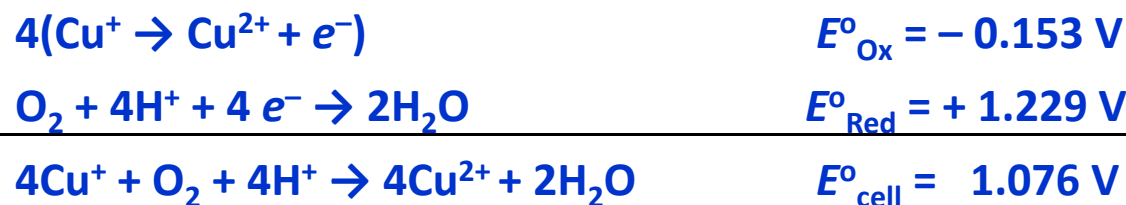
Cu(I)

- 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 CN^- , $\text{S}_2\text{O}_3^{2-}$, and 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, *Cu(I)* is readily oxidized to *Cu(II)* in the presence of oxygen:



- Moreover, *Cu(I)* undergoes *spontaneous disproportionation* (auto-redox):



- 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 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:



$$E^{\circ}_{\text{cell}} = + 0.442 \text{ V}$$



$$E^{\circ}_{\text{cell}} = + 0.442 \text{ V}$$

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



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



- 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.

- The equilibrium can be displaced in either direction:

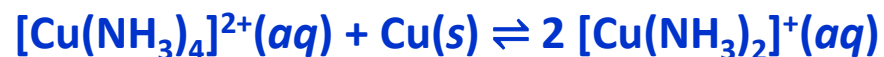


Anions or bridging ligands that form complexes with Cu^+ may stabilize Cu^+ so long as they do not form more stable complexes with Cu^{2+} .

- 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 $\text{CuCl}(s)$ 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:**



- The copper(II) complex is favored by the chelating nature of en. 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

- **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.**



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



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