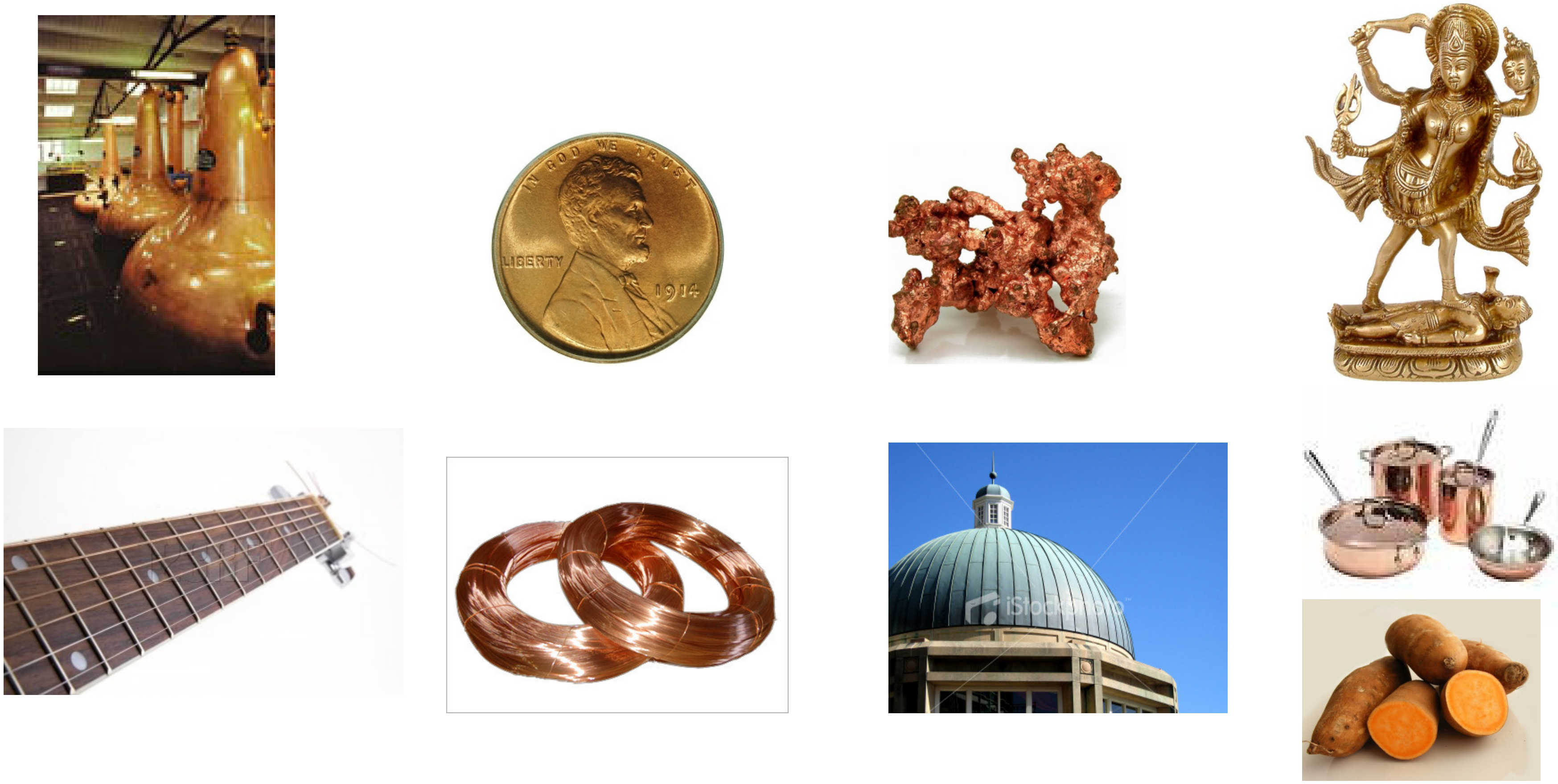
Copper Chemistry

Cu : $1s^22s^22p^63s^23p^64s^13d^{10}$



F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., John Wiley, New York, pp. 855-864.

- 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).

$$\mathbf{K} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1$$

$$\downarrow \; 4.34 \text{ eV}$$

$$\mathbf{K}^+ : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6$$

$$\downarrow \; 31.63 \text{ eV}$$

$$\mathbf{K}^{\mathbf{2+}} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^5$$

$$\mathbf{Cu} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1\, 3d^{10}$$

$$\downarrow \; 7.73 \text{ eV}$$

$$\mathbf{Cu}^+ : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}$$

$$\downarrow \; 20.29 \text{ eV}$$

$$\mathbf{Cu}^{\mathbf{2+}} : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^9$$

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 3*d* subshell permits *d-d* state-to-state electronic transitions, which causes color ***(typically blue or green)***

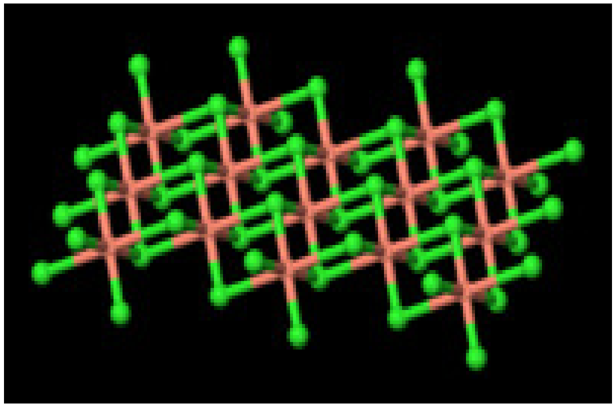
vs.

Cu(I)

- Cu(I) is an ***unstable*** state of copper
- Configuration $3d^{10}$ with no unpaired electrons ***(diamagnetic)***
- Complete 3*d* subshell precludes *d-d* state-to-state transitions, so Cu(I) is ***colorless*** like isoelectonic 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 $CuCl_2(H_2O)_2$ 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 $[Cu(H_2O)_6]^{2+}$ 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.



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 H_3O^+ $CuCl_2^-$ with concentrated hydrochloric acid. It also dissolves in solutions containing CN^-, $S_2O_3^{2-}$, and NH_3 to give corresponding 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*:

$$\begin{array}{ll}
4(\mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+} + e^{-}) & E^{o}_{\mathrm{Ox}} = -\,0.153\ \mathrm{V} \\
\mathrm{O}_2 + 4\mathrm{H}^{+} + 4\,e^{-} \rightarrow 2\mathrm{H}_2\mathrm{O} & E^{o}_{\mathrm{Red}} = +\,1.229\ \mathrm{V} \\
\hline
4\mathrm{Cu}^{+} + \mathrm{O}_2 + 4\mathrm{H}^{+} \rightarrow 4\mathrm{Cu}^{2+} + 2\mathrm{H}_2\mathrm{O} & E^{o}_{\mathrm{cell}} = \ \ 1.076\ \mathrm{V}
\end{array}$$

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

$$\begin{array}{ll}
\mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+} + e^{-} & E^{o}_{\mathrm{Ox}} = -\,0.153\ \mathrm{V} \\
\mathrm{Cu}^{+} + e^{-} \rightarrow \mathrm{Cu} & E^{o}_{\mathrm{Red}} = +0.521\ \mathrm{V} \\
\hline
2\ \mathrm{Cu}^{+} \rightarrow \mathrm{Cu} + \mathrm{Cu}^{2+} & E^{o}_{\mathrm{cell}} = +\,0.368\ \mathrm{V}
\end{array}$$

- Thus $\Delta G°$ (= $-nFE°$) is negative, i.e. 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 $CuCl_2$(*aq*) in the presence of excess Cu.
- *Synthesis takes advantage of the stability of solid CuCl*, which makes redox between Cu and Cu^{2+} spontaneous:

$$Cu(s) + Cu^{2+}(aq) + 2Cl^{-}(aq) \rightarrow 2\ CuCl(s) \qquad E^{o}_{cell} = +0.442\ V$$

- In concentrated HCl solution, the dichlorocuprate ion, $[CuCl_2]^-$, is the actual product:

$$Cu(s) + Cu^{2+}(aq) + 4\ Cl^-(aq) \rightleftharpoons 2\ [CuCl_2]^-(aq)$$

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

$$[CuCl_2]^-(aq) \rightleftharpoons CuCl(s) + Cl^-(aq)$$

- Conversely, if CuCl(*s*) is added to a chloride solution, it will dissolve due to the driving force of forming the $[CuCl_2]^-(aq)$ 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* $[CuCl_2]^-(aq)$ *drives the equilibrium to the right* (LeChatelier's Principle).
- By contrast, when CuCl(*s*) is treated with ethylenediamine (en) Cu^+ is oxidized to Cu^{2+} because *the bis-ethylenediamine copper(II) complex is more stable than the copper(I) complex:*

$$2\ CuCl(s) + 2\ en \rightleftharpoons [Cuen_2]^{2+}(aq) + Cu(s) + 2\ Cl^-(aq)$$

- The copper(II) complex is favored by the chelating nature of *en*. With non-chelating ligands such as NH_3 and pentamethylenediamine $[H_2N\text{-}(CH_2)_5\text{-}NH_2]$ the copper(I) complex is favored:

$$[Cu(NH_3)_4]^{2+}(aq) + Cu(s) \rightleftharpoons 2\ [Cu(NH_3)_2]^+(aq)$$

Copper(I) Iodide

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

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2$$

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

$$2I^{-} \rightarrow I_2 + 2e^{-} \qquad E^{o}_{Ox} = -0.54\text{ V}$$

$$2(Cu^{2+} + I^{-} + e^{-} \rightarrow CuI) \qquad E^{o}_{Red} = +0.88\text{ V}$$

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2 \qquad E^{o}_{cell} = +0.34\text{ V}$$