# The Copper Cycle

## Introduction

Many aspects of our lives involve chemical reactions—from the batteries that power our cars and cell phones to the thousands of processes occurring within our bodies. We cannot even begin to identify the millions of chemical reactions occurring around us all the time; yet, most of these reactions can be classified into one of **three main types** of chemical reactions: **precipitation** reactions, **acid-base neutralization** reactions, and **oxidation-reduction** (also called "**redox**") reactions.

## Aqueous Solutions(aq)

Many reactions occur in an **aqueous** environment (i.e., in a solution where ions and compounds are dissolved in water). When we indicate that a reactant or product has the physical state *(aq)*, we mean the **substance is dissolved in water**. When an ionic compound is in aqueous solution, the individual ions are present in solution; for example, NaCl*(aq)* exists as $Na^+$ and $Cl^-$ ions moving around in water.

## Solubility Rules

Many ionic compounds are *soluble*—i.e., they dissolve in water. Others generally do not dissolve in water and are considered *insoluble*. To determine if an ionic compound is soluble—i.e., will dissolve—in water, we use the Solubility Rules:

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### Solubility Rules for Ionic Compounds in Water

The **compound is SOLUBLE** if it has:

1. $Li^+$, $Na^+$, $K^+$, or $NH_4^+$ ion (**ALWAYS!**)

2. $C_2H_3O_2^-$, $NO_3^-$, $ClO_4^-$

3. $Cl^-$, $Br^-$, or $I^-$, **except compounds with $Ag^+$, $Pb^{+2}$, and $Hg_2^{+2}$ are insoluble**

4. $SO_4^{2-}$ **except compounds with $Ag_2SO_4$, $CaSO_4$, $SrSO_4$, $BaSO_4$, $PbSO_4$, and $Hg_2SO_4$ are insoluble**

The **compound is INSOLUBLE** if it has:

5. $CO_3^{2-}$, $CrO_4^{2-}$, $PO_4^{3-}$, **except compounds with $Li^+$, $Na^+$, $K^+$, $NH_4^+$ are soluble**

6. $S^{2-}$, **except compounds with $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$ are soluble**

7. Hydroxide ion, $OH^-$, **except compounds with $Li^+$, $Na^+$, $K^+$, $NH_4^+$ are soluble**

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The Solubility Rules indicate which compounds are soluble, and thus are represented as aqueous: e.g., KI*(aq)*, BaCl$_2$*(aq)*, NaOH*(aq)*, etc. The Solubility Rules also indicate which compounds are **insoluble**—i.e., do not dissolve in water and remain as solids: e.g. BaSO$_4$*(s)*, AgCl*(s)*, CaCO$_3$*(s)*, etc.

## Precipitation Reaction

For example, consider the reaction between aqueous lead(II) nitrate with aqueous potassium bromide, as shown below:

$$Pb(NO_3)_2(aq) \ + \ KBr(aq) \ \rightarrow \ PbBr_2 \ + \ KNO_3$$
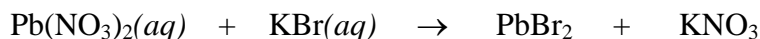
> Note that the chemical formulas for the products formed are based on their charges, not how they appear on the reactant side of the chemical equation.

Based on Solubility Rules #4 and #1, we find that PbBr$_2$ is insoluble and KNO$_3$ is soluble. Thus, the **complete, balanced** equation is:

$$Pb(NO_3)_2(aq) \ + \ 2 \ KBr(aq) \ \rightarrow \ PbBr_2(s) \ + \ 2 \ KNO_3(aq)$$
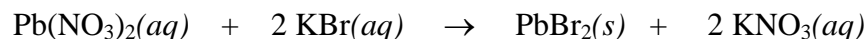
We can cancel the spectator ions from the ionic equation and write the net ionic equation:

$$Pb^{2+}(aq) \ + \ 2\ Br^-(aq) \ \rightarrow \ PbBr_2(s)$$
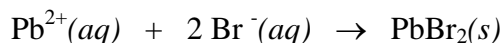
This reaction produces a cloudy mixture with small particles of the solid suspended in the solution. When enough solid has formed, it will begin to settle at the bottom of the beaker. Thus, a clear solution becoming cloudy when another solution is added is often taken as experimental evidence of a solid or precipitate forming.

## *Acids and Bases*

In general, *acids* are compounds that *produce hydrogen ions ($H^+$),* also called *protons*. Acids can also be defined as substances that produce *hydronium ions ($H_3O^+$)*, which is a hydrogen ion combined with a water molecule: $H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$. The two equations below both represent the ionization of hydrochloric acid, HCl*(aq)*:

$$HCl(aq) \ \rightarrow \ H^+(aq) \ + \ Cl^-(aq)$$

$$HCl(aq) \ + H_2O(l) \ \rightarrow \ H_3O^+(aq) \ + \ Cl^-(aq)$$
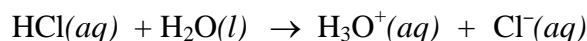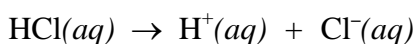
Acids are usually easy to recognize since their formulas start with H—e.g. HCl*(aq)*, HNO$_3$*(aq)*, and H$_2$SO$_4$*(aq)* are all acids. *Note that the physical state aqueous, (aq), must be included to distinguish an acid from other forms of a substance. For example, the formula "HCl" can also be used for hydrogen chloride gas, HCl(g), so to indicate hydrochloric acid, one must specify HCl(aq).*

For now, *bases* are compounds that *produce hydroxide ions ($OH^-$ )* when dissolved in water. The dissociation of sodium hydroxide, NaOH, is shown below:

$$NaOH(aq) \ \rightarrow \ Na^+(aq) \ + \ OH^-(aq)$$
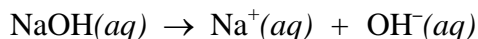
### *Acid-Base Neutralization Reactions*

In an acid-base neutralization reaction, an acid reacts with a base to produce water and a salt (an ionic compound):

$$\underset{\text{acid}}{HCl(aq)} \ + \ \underset{\text{base}}{NaOH(aq)} \ \rightarrow \ \underset{\text{water}}{H_2O(l)} \ + \ \underset{\text{salt}}{NaCl(aq)}$$
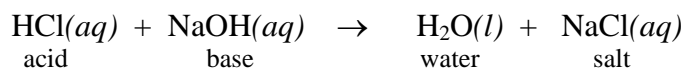
Because water is always formed, acids will always react with bases, regardless of whether the salt is soluble or insoluble.

When carrying out an acid-base neutralization reaction in the laboratory, we observe that most solutions of acids and bases are colorless, and the resulting water and soluble salt solutions are also colorless. Thus, it is impossible to monitor the progress of an acid-base reaction based solely on the appearance of the solutions. To help us monitor acid-base reactions, we use **litmus paper** to determine if a solution is acidic or basic. Litmus paper changes color depending on the presence of $H^+$ or $OH^-$ ions in the substance being tested. Blue litmus paper turns **red** in **acidic** solutions containing $H^+$ ions, and red litmus paper turns **blue** in **basic** solutions containing $OH^-$ ions.

## *Oxidation-Reduction (Redox) Reactions*

The third type of chemical reaction is the **oxidation-reduction** (or **redox**) **reaction**. Redox reactions include combination, decomposition, single-replacement, and combustion reactions. By definition, a redox reaction involves the transfer of electrons. The substance that *loses electrons* (the oxidation

number **increases** from reactants to products) is **oxidized**, and the substance that *gains electrons* (the oxidation number **decreases**) is **reduced**. To identify the substance oxidized and the substance reduced, one must determine the *oxidation state* or *oxidation number* of **each** element in the reactants and products. This is covered in chapter 4, section 6, but will be omitted here.

The combination reaction between iron metal and oxygen gas to produce rust, $Fe_2O_3(s)$, can be represented by the following balanced chemical equation:

$$4\ Fe(s) \quad + \quad 3\ O_2(g) \quad \rightarrow \quad 2\ Fe_2O_3(s)$$
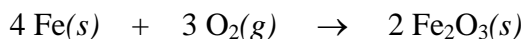
Since Fe*(s)* and $O_2(g)$ are the naturally occurring forms of iron and oxygen, then the oxidation number for these atoms is zero. Since oxygen's charge is usually -2 in an ionic compound, the iron's charge must be +3 in $Fe_2O_3$. The oxidation states for each element is shown above the chemical formula in the equation below:

$$\overset{0}{4\ Fe(s)} \quad + \quad \overset{0}{3\ O_2(g)} \quad \rightarrow \quad \overset{+3\ -2}{2\ Fe_2O_3(s)}$$
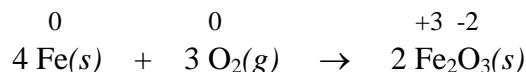
Note how Fe*(s)* loses 3 electrons to become $Fe^{+3}$ in the product while $O_2(g)$ gains 2 electrons to become $O^{-2}$. Thus, the **oxidation number increases** for Fe (it **loses electrons**), and it is **oxidized**. The **oxidation number decreases** for O (it **gains electrons**), and it is **reduced**.

The change in oxidation number for oxidation and reduction is summarized below:

- **Oxidation: When electrons are lost,** the **oxidation number increases.**
- **Reduction: When electrons are gained,** the **oxidation number decreases.**

Since the **reactant oxidized**, Fe*(s)*, caused the reduction of $O_2(g)$, Fe*(s)* serves as the **reducing agent**. Since the **reactant reduced**, $O_2(g)$, caused the oxidation of Fe*(s)*, $O_2(g)$ serves as the **oxidizing agent**. This is summarized below:

- The **reactant oxidized** is the **reducing agent** (also called the reductant).
- The **reactant reduced** is the **oxidizing agent** (also called the oxidant).

Consider another reaction:   $Ca(s)\ +\ H_2O(l) \quad \rightarrow \quad H_2(g)\ +\ Ca(OH)_2(aq)$
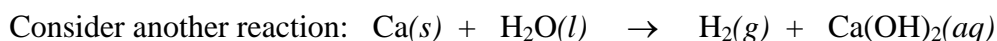
Use oxidation numbers to determine what reactant is oxidized, what reactant is reduced, what is the oxidizing agent, and what is the reducing agent. The oxidation number for each element in the reactants and products is shown below:

$$\overset{0}{Ca(s)}\ +\ \overset{+1\ -2}{H_2O(l)} \quad \rightarrow \quad \overset{0}{H_2(g)}\ +\ \overset{+2\ -2\ +1}{Ca(OH)_2(aq)}$$
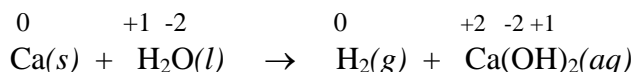
Ca*(s)* loses electrons to become $Ca^{+2}(aq)$ while the $H^+$ in $H_2O(l)$ gains electrons to form $H_2(g)$. Thus, Ca*(s)* is oxidized and serves as the reducing agent while the $H^+$ in $H_2O(l)$ is reduced, and $H_2O(l)$ serves as the oxidizing agent.

Note:   The $H^+$ in $H_2O(l)$ is reduced, but the entire *reactant*, $H_2O(l)$—not just the $H^+$—is indicated as the oxidizing agent. Note that the reaction also includes hydrogen, $H_2(g)$, on the product side. However, since hydrogen, $H_2(g)$, is a *product*, it cannot be the substance that was oxidized or reduced.

The Chemistry behind each step of the Copper Cycle:

## *Step I: Chemistry*

The different copper species obtained in each part is shown in Equation 1 below:

$$Cu(s) \xrightarrow{\textbf{Part I}} Cu^{2+}(aq) \xrightarrow{\textbf{Part II}} Cu(OH)_2(s)$$

$$\xrightarrow{\textbf{Part III}} \underset{\text{blue}}{CuO(s)} \xrightarrow{\textbf{Part IV}} Cu^{2+}(aq) \xrightarrow{\textbf{Part V}} Cu(s)$$
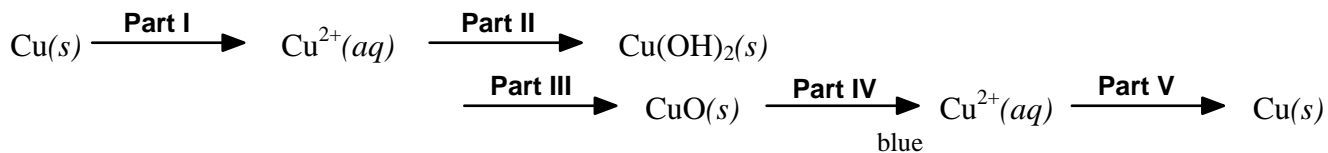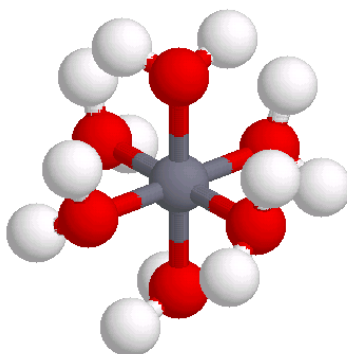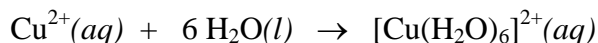
**Figure 1 (below).** When the reaction mixture is diluted with water, the $Cu^{2+}$ ions are hydrated (surrounded by water) to form the octahedral complex ion, $[Cu(H_2O)_6]^{2+}$, as shown below. Six water molecules (shown as red O and white H atoms) are bonded to a $Cu^{2+}$ ion (shown in gray as the central atom).

$$Cu^{2+}(aq) \; + \; 6\,H_2O(l) \; \rightarrow \; [Cu(H_2O)_6]^{2+}(aq)$$



### I.  Oxidizing Copper Metal with Concentrated Nitric Acid, $HNO_3(aq)$

The first step involves transforming Cu metal to copper(II) ions, $Cu^{2+}$, using concentrated nitric acid, $HNO_3(aq)$. At the same time, the nitrate ions ($NO_3^-$) are converted to nitrogen dioxide, $NO_2$, a brown gas. The presence of $Cu^{2+}(aq)$ makes the solution blue.
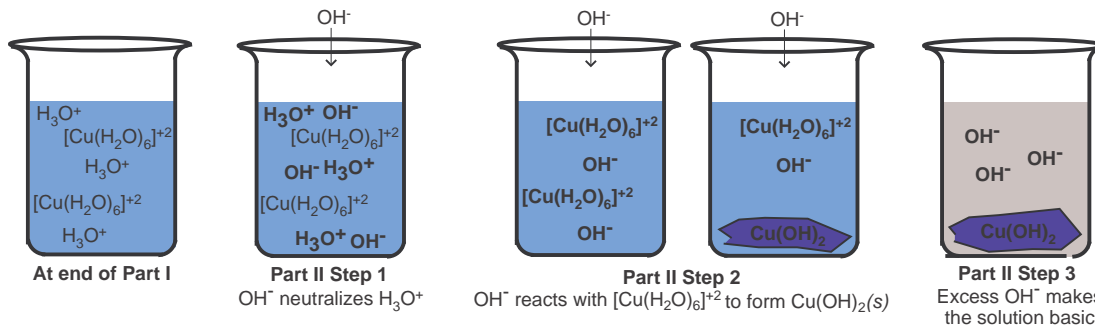
## *Step II: Chemistry*
### II.  Precipitating $Cu(OH)_2(s)$ with $NaOH(aq)$

In Part II, two reactions are carried out by adding $NaOH(aq)$. In the first reaction, the hydroxide ions ($OH^-$) from the $NaOH(aq)$ neutralize the excess hydronium ions ($H_3O^+$) left over from the previous part:

$$H_3O^+(aq) \; + \; OH^-(aq) \; \rightarrow \; 2\,H_2O(l)$$
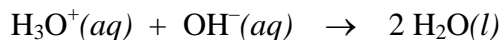
Once all the $H_3O^+$ ions are neutralized, additional $OH^-$ ions react with the $Cu^{2+}$ ion to form $Cu(OH)_2$ precipitate. Once all the $Cu^{2+}$ ions have reacted, no more precipitate forms. Adding more $OH^-$ ions makes the solution basic, so it can turn red litmus paper blue. Figure 2 on the next page shows the step-wise reaction of $Cu^{2+}$ with NaOH.

**Figure 2: Step-wise Illustration of the Precipitation of Cu(OH)₂ in Part II – Remember: [Cu(H₂O)]²⁺ indicates the same substance as Cu²⁺.**

| At end of Part I | Part II Step 1 OH⁻ neutralizes H₃O⁺ | Part II Step 2 OH⁻ reacts with [Cu(H₂O)₆]⁺² to form Cu(OH)₂(s) | | Part II Step 3 Excess OH⁻ makes the solution basic |

$H_3O^+$, $[Cu(H_2O)_6]^{+2}$, $H_3O^+$, $[Cu(H_2O)_6]^{+2}$, $H_3O^+$

$OH^-$; $H_3O^+$ $OH^-$, $[Cu(H_2O)_6]^{+2}$, $OH^-$ $H_3O^+$, $[Cu(H_2O)_6]^{+2}$, $H_3O^+$ $OH^-$

$OH^-$; $[Cu(H_2O)_6]^{+2}$, $OH^-$, $[Cu(H_2O)_6]^{+2}$, $OH^-$

$OH^-$; $[Cu(H_2O)_6]^{+2}$, $OH^-$, $Cu(OH)_2$

$OH^-$; $OH^-$, $OH^-$, $Cu(OH)_2$

**1ˢᵗ Beaker**: At the end of Part I, hydrated copper complex, $Cu^{2+}$ are present, making the solution blue, and excess hydronium ions ($H_3O^+$) remain from the nitric acid used.

**2ⁿᵈ Beaker**: Adding NaOH*(aq)* to the blue solution results in the $OH^-$ ions neutralizing the $H_3O^+$ ions to form water: $H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O(l)$. The $Na^+$ ions and resulting water molecules are not shown.

**3ʳᵈ and 4ᵗʰ Beakers**: Once all the $H_3O^+$ are neutralized, adding more NaOH*(aq)* results in the $OH^-$ ions reacting with the $Cu^{2+}$ to form the blue $Cu(OH)_2(s)$ precipitate shown at the bottom of the beaker. Water molecules released from the complex ion are not shown.

**5ᵗʰ Beaker**: When all of the $Cu^{2+}$ ions have been converted to $Cu(OH)_2(s)$ precipitate, adding more NaOH*(aq)* results in unreacted $OH^-$ ions in solution, which makes the solution basic. Red litmus paper can be used to confirm the solution is basic. Note that the solution is no longer blue since no $Cu^{2+}$ ions are present in the solution.

## *Step III: Chemistry*
### III. Converting solid Cu(OH)₂ to solid CuO

In Part III of the sequence, the reaction mixture is heated. This transforms the $Cu(OH)_2$ precipitate to CuO precipitate.

The CuO precipitate is separated from the solution, called the **supernatant liquid**, using a method called **gravity filtration**. The mixture is filtered using a filter funnel, and the solid is collected on filter paper. The supernatant liquid runs through the filter paper and collects in a beaker. This resulting filtered solution is called the **filtrate**.

## *Step IV: Chemistry*
### IV. Dissolving CuO*(s)* with sulfuric acid, H₂SO₄*(aq)*

In Part IV, the CuO precipitate is dissolved using sulfuric acid, $H_2SO_4(aq)$. This redox reaction returns copper to its aqueous phase.

## Step V: Chemistry
### V. Reducing $Cu^{2+}$ ions with Zinc Metal

In Part V, zinc metal (Zn) is added to the copper solution to convert the copper ions back to copper metal, Cu*(s)*. The resulting solution will contain colorless zinc ions, $Zn^{2+}$*(aq)* and copper solid. Visible evidence of this reaction is observed as bubbles of gas being released from the solution. (Since the $H_3O^+$ ions do not dissolve the Cu metal, the amount of copper yielded is not affected by excess acid.) Identify the gas displaced from the acid in this reaction.

When the solution becomes colorless, all of the $Cu^{2+}$ ions have been converted to Cu metal.

All of the excess Zn metal is also converted to $Zn^{2+}$ ion by the excess $H_3O^+$ ions from the sulfuric acid, $H_2SO_4$*(aq)*,used to dissolve the CuO precipitate in Part IV.

Once all the Zn metal is dissolved, the Cu metal can be isolated by **decanting**, or **pouring off**, the supernatant liquid. The Cu will then be rinsed, dried, and weighed as described in the procedure.