

MAROOCHYDORE SHS



Metal Extraction Chemistry

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Student booklet

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Worksheet 2.1 OVERVIEW - METAL EXTRACTION CHEMISTRY

A solid element or compound which occurs naturally in the Earth's crust is called a <u>mineral</u>. A mineral which contains a high enough percentage of a metal for economic extraction is called a metal <u>ore</u>. The most common metal ores are <u>oxides</u> (such as Al_2O_3) and <u>sulfides</u> (such as PbS). Sulfides are the oldest ores, formed in the Earth's history when there was a lot of sulfur from volcanic activity. Oxides formed later when photosynthesis in plants released large amounts of oxygen into the atmosphere. Metal ore deposits are a finite resource (there are only a certain amount of them) and non-renewable (once used, they are gone and will not be replaced).

TABLE 21.1	Principal Types of Minerals
Туре	Minerals
Native metals	Ag, Au, Bi, Cu, Pd, Pt
Carbonates	BaCO ₃ (witherite), CaCO ₃ (calcite), MgCO ₃ (magnesite),
	 CaCO₃·MgCO₃ (dolomite), PbCO₃ (cerussite), ZnCO₃ (smithsonite)
Chromate	$PbCrO_4$ (crocoite)
Halides	CaF ₂ (fluorite), NaCl (halite), KCl (sylvite), Na ₃ AlF ₆ (cryolite)
Hydroxides	$Mg(OH)_2$ (brucite), $Mg_3(Si_4O_{10})(OH)_2$ (talc)
Oxides	Al ₂ O ₃ (corundum), Fe ₂ O ₃ (hematite), Fe ₃ O ₄ (magnetite), Cu ₂ O (cuprite), MnO ₂ (pyrolusite), SnO ₂ (cassiterite), TiO ₂ (rutile), ZnO (zincite)
Phosphates	$Ca_3(PO_4)_2$, $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite)
Silicates	$Be_3Al_2Si_6O_{18}$ (beryl), $ZrSiO_4$ (zircon), $NaAlSi_2O_8$ (albite)
Sulfides	Ag ₂ S (argentite), CdS (greenockite), Cu ₂ S (chalcocite), HgS (cinnabar), PbS (galena), ZnS (sphalerite)
Sulfates	BaSO ₄ (barite), CaSO ₄ (anhydrite), PbSO ₄ (anglesite), SrSO ₄ (celestite), MgSO ₄ ·7H ₂ O (epsomite)

In order to extract the metal, the ore or compound of the metal must undergo a process called reduction (i.e. the positive metal ion gains electrons to form the neutral metal atom). Preliminary reactions may be necessary to convert the ore into a

chemical state more suitable for reduction. Often an ore is <u>roasted</u> (heated in air) to drive off volatile impurities and/or convert the sulphide and carbonate forms of the ore to oxides, which more readily undergo reduction. Examples are

$$CaCO_{3(s)} \ \rightarrow \ CaO_{(s)} \ + \ CO_{2(g)}$$

 $2 \ \text{PbS}_{(s)} \ \ + \ \ 3 \ \text{O}_{2(g)} \ \rightarrow \ \ 2 \ \text{PbO}_{(s)} \ \ + \ \ 2 \ \text{SO}_{2(g)}$

Note that in these reactions the metal ion does not undergo reduction.

The reduction itself can be done in several ways and generally speaking the method of extraction used depends on the position of the metal in the reactivity series

The reactivity series of metals is shown with two non-

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metals, carbon and hydrogen, to help predict which method could be used to extract a metal.

A metal <u>low</u> in the activity series is considered relatively unreactive – it does not lose it's valence electrons easily (not undergo oxidation readily).

A metal <u>high</u> in the series is considered reactive – meaning it readily loses it's valence electrons (undergoes oxidation readily) to more electronegative elements, such as those metals lower than it in the series.

As a general rule any element higher in the series can displace any other lower element. Review the results of the reactivity of metals experiment to confirm this.

Some metals are so unreactive (bottom of the activity series of metals) that they do not readily combine with oxygen in the air or any other element present in the Earth's crust, and so can be found as the metal itself. For example gold (and sometimes copper and silver) and no chemical separation or extraction is needed. In fact all the metals below hydrogen can be found as the 'free' or 'native' element.

metals below hydrogen can be found as the 'free' or 'native' element.
 Metals below carbon can be extracted by heating the oxide with carbon. Carbon, or its combustion product carbon monoxide will displace the less reactive metals in a smelter or blast furnace. Carbon acts as a reducing agent and essentially provides electrons for the reduction of the metal ion to metal atom. Examples (M = Metal) of the reactions that occur during smelting...

Metals above carbon in the reactivity series cannot usually be extracted with carbon or carbon monoxide. They are usually extracted by electrolysis of the purified molten ore or other suitable compound e.g. aluminium from molten aluminium oxide. The ore or compound must be molten or dissolved in a solution in an electrolysis cell to allow free movement of ions (electrical current). Examples (M = Metal) include...

Other methods are used in special cases using the displacement rule. A more reactive metal can be used to displace and extract a less reactive metal but these are costly processes since the more reactive metal also has to be produced in the first place! <u>Eg.</u> <u>Titanium</u>. Examples include...

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TABLE 21.2 Reduction Processes for Some Common Metals				
	Metal	Reduction Process		
tals	Lithium, sodium, potassium, magnesium, calcium	Electrolytic reduction of the molten chloride		
of me	Aluminum	Electrolytic reduction of anhydrous oxide (in molten cryolite)		
sing activity	Chromium, manganese, titanium, vanadium, iron, zinc	Reduction of the metal oxide with a more electropositive metal, or reduction with coke and carbon monoxide		
Decrea	Mercury, silver, platinum, copper, gold	These metals occur in the free (uncombined) state or can be obtained by roasting their sulfides		

Questions:

- 1. Write definitions for: mineral, ore, reactivity series of metals, reactive (metal reactivity).
- 2. Which metal is found in the largest number of combined states (ores)? Check table 21.1, and list the different ores with their names (common and scientific).
- 3. Why is reduction an essential part of metal extraction chemistry?
- 4. What preliminary reactions may be necessary prior to the reduction of a metal ore? List examples of such reactions.
- 5. List the four main methods used to extract metals from their ores. Beside each write down the main factor that determines if this method is suitable for a particular metal.
- 6. Copper exists in nature in both the free (elemental) and combined (oxidized) states, whereas aluminium is only ever found in the combined state. Explain
- 7. Explain how you would obtain Zinc from sphalerite (ZnS)? Justify your choice of process by providing the reason behind your choice.
- Consider the electrolytic procedure for purifying copper described in figure 21.1. Suppose that a copper sample to be purified in this manner had the following impuritites: Fe, Ag, Zn, Au, Sn, Pt, and Pb. Which of the metals will be oxideised and dissolved into the solution; and which will not be oxidized and fall as sludge to the bottom?
- 9. Which of the following componds would require electrolysis to yield the free metals: Ag₂S, CaCl₂, KCl, Fe₂O₃, Al₂O₃, and TiCl₄? Which could be smelted in a blast furnace?



FIGURE 21.1 The electrolytic purification of copper. The more electropositive metals, such as zinc and iron, are oxidized at the anode and enter the solution as Fe^{2+} and Zn^{2+} , while copper is transferred from the anode to the cathode via Cu^{2+} ions. The less electropositive metals, such as gold and silver, are not oxidized at the anode.

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- 10. Outline the reactions that would occur for the production of iron from Iron oxide (Fe_2O_3) in a blast furnace (smelting)?
- 11. Although iron is only about 2/3rd as abundant as aluminium in the earth's crust, mass for mass it costs only about 1/4 as much to produce. Why?

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Worksheet 2.2: METALLURGY OF COPPER

Student activity sheet

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Common copper ores include:

Copper pyrite or chalcopyrite (CuFeS₂). Chalocite (Cu₂S) or copper glance. Malachite green [CuCO₃.Cu(OH)₂].Azurite blue [2CuCO₃.Cu(OH)₂]. Bornite ($3Cu_2S$.Fe₂S₃) or peacock ore. Melaconite (CuO) etc.

EXTRACTION OF COPPER FROM SULPHIDE ORE

Large amount of copper are obtained from copper pyrite (CuFeS₂) by smelting. Ores containing 4% or more copper are treated by smelting process. They are first concentrated by froth flotation. Very poor ores are treated by hydro-metallurgical process.

EXTRACTION OF COPPER BY SMELTING PROCESS

ROASTING

The concentrated ore is first roasted in a furnace in the presence of a current of air. Sulphur is oxidized to SO_2 and impurities of arsenous and antimony are removed as volatile oxides. The following reactions take place.

$2CuFeS_2$	+	O ₂	\rightarrow	Cu_2S	+	2FeS	+	SO ₂
S	+	O ₂	\rightarrow	SO ₂				
4As	+	3O ₂	\rightarrow	As_2O_3				
4Sb	+	3O ₂	\rightarrow	$2Sb_2O_2$	3			

<u>SMELTING</u>

The roasted ore is mixed with coke and silica (sand) SiO_2 and is introduced in to a blast furnace to produce a molten matte (mixture) of copper. The hot air is blasted through the molten matte and converts Cu_2S partly into Cu_2O which reacts with remaining Cu_2S to give molten copper.

FeS and any FeO in the matte is converted to ferrous silicate (FeSiO₃).

FeSiO₃ (slag) floats over the molten matte of copper.

The copper so obtained is called "Blister copper" because, as it solidifies, SO_2 hidden in it escapes out producing blister on its surface.

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IMPURITIES IN BLISTER COPPER AND THEIR EFFECTS

Blister copper is 99% pure. It contains impurities, mainly iron but little amount of As, Zn, Pb, Ag and Au may also be present. These impurities adversely affect the electrical as well as mechanical properties of copper. Therefore, they must be removed.

REFINING OF COPPER

Blister copper is refined by electrolysis. Blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes. The electrolyte is copper sulphate (CuSO₄) mixed with a little amount of H_2SO_4 to increase the electrical conductivity. During electrolysis, pure copper is deposited on the cathode plates and impurities which are soluble and fall to the bottom of the cell as anode mud or sludge.

ELECTROCHEMICAL CHANGES DURING ELECTROLYSIS

		Cu	\rightarrow	Cu ⁺²	+	2e-	(at the anode)
Cu ⁺²	+	2e-	\rightarrow	Cu			(at the cathode)

This electrically refined copper is 100% pure.



Information adapted from www. citycollegiate.com/dblock4.htm - metallurgy of copper

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Questions

1. Copy out each of the reactions listed above for the extraction of copper from chalcopyrite. For each of these reactions assign oxidation numbers and identify which (if any) elements have undergone oxidation or reduction.

2. The smelting process is used for ore bodies over 4% copper mineral. Copper leaching (a hydro-metallurgical process) is used for ores below this (usually copper oxide ores). Discuss the advantages and disadvantages of both processes and why smelting and Leaching are used for the different ores.

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Extracting iron from iron ore using a Blast Furnace

Introduction

The common ores of iron are both iron oxides, and these can be reduced to iron by heating them with carbon in the form of coke. Coke is produced by heating coal in the absence of air.

Coke is cheap and provides both the reducing agent for the reaction and also the heat source.

<u>Iron ores</u>

The most commonly used iron ores are *haematite* (US: hematite), Fe₂O₃, and *magnetite*, Fe₃O₄.

<u>The Blast Furnace</u>

<u>The heat source</u>

The air blown into the bottom of the furnace is heated using the hot waste gases from the top. Heat energy is valuable, and it is important not to waste any.

The coke (essentially impure carbon) burns in the blast of hot air to form carbon dioxide - a strongly exothermic reaction. This reaction is the main source of heat in the furnace.



The reduction of the ore

C + O₂ _____ CO₂

At the high temperature at the bottom of the furnace, carbon dioxide reacts with carbon to produce carbon monoxide.



It is the carbon monoxide which is the main reducing agent in the furnace.

Fe203 + 3C0 _____ 2Fe + 3C02

In the hotter parts of the furnace, the carbon itself also acts as a reducing agent. Notice that at these temperatures, the other product of the reaction is carbon monoxide, not carbon dioxide.

Fe₂O₃ + 3C ____ ▶ 2Fe + 3CO

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The temperature of the furnace is hot enough to melt the iron which trickles down to the bottom where it can be tapped off.

The function of the limestone

Iron ore isn't pure iron oxide - it also contains an assortment of rocky material. This wouldn't melt at the temperature of the furnace, and would eventually clog it up. The limestone is added to convert this into *slag* which melts and runs to the bottom.

The heat of the furnace decomposes the limestone to give calcium oxide.

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This is an endothermic reaction, absorbing heat from the furnace. It is therefore important not to add too much limestone because it would otherwise cool the furnace.

Calcium oxide is a basic oxide and reacts with acidic oxides such as silicon dioxide present in the rock. Calcium oxide reacts with silicon dioxide to give calcium silicate.

CaO + SiO₂ → CaSiO₃

The calcium silicate melts and runs down through the furnace to form a layer on top of the molten iron. It can be tapped off from time to time as slag.

Slag is used in road making and as "slag cement" - a final ground slag which can be used in cement, often mixed with Portland cement.

<u>Cast iron</u>

 \leq The molten iron from the bottom of the furnace can be used as *cast iron*.

Cast iron is very runny when it is molten and doesn't shrink much when it solidifies. It is therefore ideal for making castings - hence its name. However, it is very impure, containing about 4% of carbon. This carbon makes it very hard, but also very brittle. If you hit it hard, it tends to shatter rather than bend or dent.

Cast iron is used for things like manhole covers, guttering and drainpipes, cylinder blocks in car engines, Aga-type cookers, and very expensive and very heavy cookware.

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Most of the molten iron from a Blast Furnace is used to make one of a number of types of steel. There isn't just one substance called steel - they are a family of alloys of iron with carbon or various metals. More about this later . . .

--- Steel-making: the basic oxygen process

Impurities in the iron from the Blast Furnace include carbon, sulphur, phosphorus and silicon. These have to be removed.
 Berneval of sulphur.

Removal of sulphur

Sulphur has to be removed first in a separate process. *Magnesium powder* is blown through the molten iron and the sulphur reacts with it to form magnesium sulphide. This forms a slag on top of the iron and can be removed.



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Removal of carbon etc

The still impure molten iron is mixed with scrap iron (from recycling) and *oxygen* is blown on to the mixture. The oxygen reacts with the remaining impurities to form various oxides.

The carbon forms carbon monoxide. Since this is a gas it removes itself from the iron. This carbon monoxide can be cleaned and used as a fuel gas.

Elements like phosphorus and silicon react with the oxygen to form acidic oxides. These are removed using *quicklime (calcium oxide)* which is added to the furnace during the oxygen blow. They react to form compounds such as calcium silicate or calcium phosphate which form a slag on top of the iron.

Types of iron and steel

Cast iron has already been mentioned above. This section deals with the types of iron and steel which are produced as a result of the steel-making process.

Wrought iron

If all the carbon is removed from the iron to give high purity iron, it is known as wrought iron. Wrought iron is quite soft and easily worked and has little structural strength. It was once used to make decorative gates and railings, but these days mild steel is normally used instead.

Mild steel

 \leq Mild steel is iron containing up to about 0.25% of carbon. The presence of the carbon makes the steel stronger and harder than pure iron. The higher the percentage of carbon, the harder the steel becomes.

Mild steel is used for lots of things - nails, wire, car bodies, ship building, girders and bridges amongst others.

S High carbon steel

High carbon steel contains up to about 1.5% of carbon. The presence of the extra carbon makes it very hard, but it also makes it more brittle. High carbon steel is used for cutting tools and masonry nails (nails designed to be driven into concrete blocks or brickwork without bending). You have to be careful with high carbon steel because it tends to fracture rather than bend if you mistreat it.

	iron with	special properties	uses include
stainless steel	Cr and Ni	resists corrosion	cutlery, cooking utensils, kitchen sinks, industrial equipment for food and drink processing
titanium steel	titanium	Withstands high temp	gas turbines, spacecraft
manganese steel	manganese	very hard	rock-breaking machinery, some railway track (e.g. points), military helmets

Special steels These are iron alloyed with other metals. For example:

Modified from article sourced: <u>http://www.chemguide.co.uk/inorganic/extraction/iron.html</u> © Jim Clark 2005

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Questions
 1. Copy out each of the reactions listed above for the extraction of Iron from Iron Oxide ore. Do this for both the Haematite ore (as described above) and the Magnetite ore (Fe₃O₄). For each of these reactions assign oxidation numbers and identify which (if any) elements have undergone oxidation or reduction)

- 2. What reaction generates most of the heat necessary for the blast furnace? Is this a redox reaction?
- 3. List some of the materials which still have to be removed from the molten Iron after it has been extracted? Look carefully at the processes used to remove these impurities. Are these redox reactions?

4. Iron is not one of the most common metals in the earth's crust yet it is one of the cheapest metals to buy. Suggest a reason for this.





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Worksheet 2.4: EXTRACTING ALUMINIUM FROM BAUXITE

Introduction

Aluminium is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The temperatures needed are too high to be economic.

Instead, it is extracted by electrolysis. The ore is first converted into pure aluminium oxide by the Bayer Process, and this is then electrolysed in solution in molten cryolite - another aluminium compound. The aluminium oxide has too high a melting point to electrolyse on its own.

Aluminium ore

The usual aluminium ore is **bauxite**. Bauxite is essentially an impure aluminium oxide. The major impurities include iron oxides, silicon dioxide and titanium dioxide.

Purifying the aluminium oxide - the Bayer Process

<u> <u> <u> Reaction with sodium hydroxide solution</u> </u></u>

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution. The concentration, temperature and pressure used depend on the source of the bauxite and exactly what form of aluminium oxide it contains. Temperatures are typically from 140°C to 240°C; pressures can be up to about 35 atmospheres.

High pressures are necessary to keep the water in the sodium hydroxide solution liquid at temperatures above 100°C. The higher the temperature, the higher the pressure needed.

With hot concentrated sodium hydroxide solution, aluminium oxide reacts to give a solution of sodium tetrahydroxoaluminate.

Al2O3 + 2NaOH + 3H2O - 2NaAl(OH)4

The impurities in the bauxite remain as solids. For example, the other metal oxides present tend not to react with the sodium hydroxide solution and so remain unchanged. Some of the silicon dioxide reacts, but goes on to form a sodium aluminosilicate which precipitates out.

All of these solids are separated from the sodium tetrahydroxoaluminate solution by filtration. They form a "red mud" which is just stored in huge lagoons.

Precipitation of aluminium hydroxide

The sodium tetrahydroxoaluminate solution is cooled, and "seeded" with some previously produced aluminium hydroxide. This provides something for the new aluminium hydroxide to precipitate around.

NaAI(OH)4 AI(OH)3 + NaOH

Formation of pure aluminium oxide

Aluminium oxide (sometimes known as alumina) is made by heating the aluminium hydroxide to a temperature of about 1100 - 1200°C.

2AI(OH)3 _____ AI2O3 + 3H2O

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Although the carbon lining of the cell is labelled as the cathode, the effective cathode is mainly the molten aluminium that forms on the bottom of the cell.

Molten aluminium is syphoned out of the cell from time to time, and new aluminium oxide added at the top.

The cell operates at a low voltage of about 5 - 6 volts, but at huge currents of 100,000 amps or more. The heating effect of these large currents keeps the cell at a temperature of about 1000°C.

<u>The electrode reactions</u>

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These are very complicated - in fact one source I've looked at says that they aren't fully understood. For chemistry purposes at this level, they are always simplified (to the point of being wrong! - see comment below).

This is the simplification:

Aluminium is released at the cathode. Aluminium ions are reduced by gaining 3 electrons.

Al³⁺ + 3e⁻ ----- Al

Oxygen is produced initially at the anode.

2 O²⁻ _____ O₂ + 49⁻

However, at the temperature of the cell, the carbon anodes burn in this oxygen to give carbon dioxide and carbon monoxide.

Continual replacement of the anodes is a major expense.

Modified from article sourced: <u>http://www.chemguide.co.uk/inorganic/extraction/aluminium.html#top</u>

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Questions

1. Copy out each of the reactions listed above for the purification of Aluminium Oxide (Alumina). For each of these reactions assign oxidation numbers and identify which (if any) elements have undergone oxidation or reduction.

2. Write a combined redox reaction for the extraction of Aluminium from alumina. Make sure the reaction is balanced in terms of electrons gained and lost.

3. Find the following sentence in the text "However, at the temperature of the cell, the carbon anodes burn in this oxygen to give carbon dioxide and carbon monoxide". Write a balanced redox reaction for this reaction. Does this reaction contribute to the extraction of aluminium or make it more difficult?

4. List the parts of the alumina purification and aluminium extraction that appear very energy intensive and expensive to perform. Explain, in terms of it's standard electrode potential (-1.66 volts) AND it's position in the Activity series, why the procedure for aluminium production is more expensive and complicated than most metals.

EXPERIMENT 2.1

Production of Copper from its Ore: A Redox Reaction:

_Copper is often found in the form of a black ore, copper oxide, or a brassy-colored ore, copper sulphide. In both cases the metal has to be separated from its compound.

The demonstration in this experiment shows how copper can be extracted from its copper oxide ore. To obtain pure copper the oxygen has to be removed, using a process called reduction. The reducing agent used here is charcoal, a form of pure carbon. The reaction which occurs is similar to that used in the smelting of copper oxide ores in blast furnaces. The final product of the Redox reactions is carbon dioxide gas and copper metal.

Completion of the reaction can be visually assessed by the appearance of distinct copper metal. This can most easily be seen by examining the products using a x20 stereo microscope.

Materials needed:

- 1 g CuO
- 1 g charcoal
- Small amount (<0.5 gm) PbO
- Tripod
- Clay triangle
- Crucible with cover
- Bunsen burner
- Spatula
- Filter paper
- Watch glass
- Balance
- Tongs
- Matches
- Stereo microscope

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Procedure:

Copper Oxide Smelting

Measure 1g of CuO onto a piece of filter paper. On a second piece of filter paper, measure out 1g of charcoal. Transfer both chemicals into the crucible. Keep the filter paper that held the CuO, but discard the other piece. Use the spatula to stir and thoroughly mix the two chemicals in the crucible. Place the cover on the crucible, and set it in the clay triangle on the tripod. Heat strongly for 10-15 minutes. Then turn off the burner and allow the crucible to cool for 10 minutes (keeping the lid on). (See below for Lead smelting to complete during this time)

Use tongs to carefully remove the crucible cover. (Caution: It may still be hot!) Tip the contents of the crucible onto the watch glass. Use the Spatula to spread out the mixture, which will have the characteristic red colour of copper metal, but to see the metal properly examine under stereo microscope. Record your observations, especially the presence of any copper metal.

Lead Oxide Smelting

Light a match and let it burn approximately half way. Dip the charred end of the match into water and then into the PbO powder. Place the match head in the burner flame (Blue flame) and watch for the formation of tiny drops of shiny grey molten lead. Allow the match to cool, and observe the mixture under a stereo microscope. Record your observations, especially the presence of any Pb Metal.

Questions:

- 1. Describe the appearance of the copper metal produced? Explain why the copper did not form larger pieces of pure metal?
- 2. Describe the appearance of the Lead metal produced? Explain why Lead did form the shiny droplets of pure metal.
- 3. What is the oxidation number of copper in CuO, of Lead in PbO?
- 4. What is the oxidation number of the copper in the crucible after the completion of the reaction? And of the Lead on the matchstick?

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