Chapter 15 – The Analysis of A Solution for Hg (II), Cu (II), Pb (II) and Bi (II) Ions

NAME:

Lab Section:

Date: **Sign-Off:**

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Introduction

Bi -- Bismuth

Alloys of Bi, Sn and Pb have low melting points. Uses of these alloys include electrical fuses, safety plugs for boilers and automatic sprinkler systems. Bismuth subcarbonate is $(BiO)_2CO_3$ and bismuth subnitrate is $(BiO)NO_3$. Many bismuth compounds (Pepto BISmol) are used to treat gastritis and ulcers; others are used to treat skin diseases such as eczema.

As -- Arsenic

Gray As is mono-atomic and sublimes at 615° C, where it becomes tetra-atomic and takes on a tetrahedral conformation. When As vapor is cooled FAST, it becomes unstable yellow As. The yellow As is soluble in carbon disulfide and has an odor of garlic. Yellow As is very poisonous. Bronze and lead shot contains As as a hardening agent. As is used mostly as a weed killer, cattle/sheep dip and in insecticides.

Sb -- Antimony

The Egyptians used Sb for eye makeup as early as 3000 B.C. It's been used in medicines. It is a lustrous white metal and is brittle and readily pulverized. Lead plus 10-20% antimony makes "hardened lead" which is used in shrapnel, bullets and bearings. Babbit metal contains Sb (Sb, Sn and Cu) and is used as an anti-friction alloy in the production of ball bearings.

Cu -- Copper

Copper is reddish-yellow metal. It is ductile and malleable. It is the best electrical conductor of the cheap metals. It needs, though, to be very pure: impurities readily decrease its conductivity. Biologically, Cu is used with vitamin C and lysine for connective tissue biosynthesis and in the synthesis of hemoglobin. The following alloys of copper are commercially useful:

Brass	Bronze	Aluminum bronze	German silver
60-82% Cu;18-40% Zn	70-95% Cu; 1-25% Zn; 1-18% Sn	90-98% Cu; 2-10% Al	50-60% Cu; 20% Zn; 20-25% Ni

Note that in German silver there is no silver.

Sn -- Tin

Tin cans are really tin-plated steel cans. There are three forms of tin:

1) Gray Tin -- Gray tin is formed from malleable tin after prolonged exposure to temperature extremes below 13.2° C. It becomes powdery and spreads like a rash -- hence its name: tin disease or tin pest. This is a problem for organ pipes in northern Europe. The pipes are made of tin for the best sound and are regularly replaced as a result of the cold temperatures.

2) Brittle Tin -- Formed from heated malleable tin.

3) Malleable Tin -- This tin is a silver-white with bluish tinge. It is also known as white tin. When this tin is bent it emits what is called the "tin cry".

When this tin is heated it forms brittle tin. When malleable tin is exposed to temperatures below 13.2° C, it forms gray tin.

Tin is also found in different alloys:

Bronze	Type metal	Solder	Chrome plate substitute
Cu, Zn, Sn	Used in the old presses to print newspapers; Sn, Pb, Sb, Cu	Sn and Pb (the latter is being slowly replaced with Ag)	One part nickel and 2 parts tin approximate a cheap replacement for chrome plating.

Experimental

Obtain a sample of known cations for this group and procure your unknown super from the previous experiment for continuing your work through the schemes. A flow chart follows this section to clarify some of the finer points in the text.

To both solutions, confirm the approximate hydrogen ion concentration (check against red litmus) as either acid or neutral. Be sure you use your glass stirring rod to dip into the solution and then to touch to the litmus paper when checking acidity/alkalinity. Add 6M ammonia to the solutions a drop at a time until the litmus turns from red to blue. You may get a blue color in the solution that indicates the presence of Cu(II). To your basic solutions, add 2M hydrochloric acid a drop at a time with mixing/stirring until the pH is between 2 and 3 (use wide-range pH paper). Add 0.35 mL (7 drops) of 2 M hydrochloric acid. To the, now, acidic (pH of about 0.5) mixture, add 4 gtts thioacetamide (TA) and enough distilled water to make a final volume of 2.5 mL. Place the mixtures in a boiling water bath for at least 5 minutes. Remove from the bath and centrifuge the tubes.

Pour the supers off into different tubes, confirm that the pH is not below 0.5 (if it is, raise it with the dilute ammonia), add 2 gtts TA and boil, again, for 5 minutes. Separate the ppts and supers (combining as necessary to get them into one tube for the known ppt, (you don't need to keep the super from the known solution) one tube for the unknown ppt and one tube for the unknown super. Repeat no more than one more time, combining ppts and supers as above.

Wash the ppts with 1 mL of hot distilled water that contains 1 gtt 6 M nitric acid and centrifuge. Add the washing from the unknown ppt to the super you obtained in the previous paragraph. Set the unknown super aside for future use and label ❷S3. To each tube of ppt (known and unknown samples), add a half mL of 0.5M potassium hydroxide and heat for a few minutes in the boiling water bath. Centrifuge the tubes and dispose of the super – repeat the KOH washing of the ppt one more time, likewise disposing of the wash super. To the combined ppts you just obtained, add 0.25 mL of water and 0.25 mL of 6M nitric acid and warm in the warm water bath – in this reaction, you're looking for bubbling (not boiling) to occur to float elemental sulfur and sulfides to the top of the reaction mixture. After 5 minutes, if no bubbles occur, centrifuge the samples, pouring off the super into another test tube – keep both super and ppt from this step.

> To the ppts, add 6 gtts of Clorox and 2 gtts of 6M hydrochloric acid with stirring. Add 20 gtt water and heat to boiling. Now add 2 gtts tin chloride solution and centrifuge. A white, grey or black ppt is positive for mercury.
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> To the supers you saved above, pour them into their own casseroles and add 2 gtts con sulfuric acid. Heat to evaporation over a micro-flame and under a ventilatory duct or siphon (your professor will show you how to make one of these) until copious amounts of white dense fumes are billowing out. Cool and carefully add 5 gtts distilled water and scrape with your glass stirring rod to loosen the solid from the walls of the casserole. Dump into a test tube, rinse casserole twice with distilled water and pour the rinsings into the test tubes, as well. Centrifuge and pour the super into a new test tube.

To the new ppt, add a few drops of ammonium acetate solution with mixing. Centrifuge and discard the remaining ppt. Add a drop of 6M HOAc and a few drops of potassium chromate solution. A strong yellow ppt is positive for lead.

To the super you obtained at the end of the paragraph just above the previous paragraph, add concentrated ammonia until the solution is alkaline to litmus. A blue soln is positive for copper. Even though you may not see a ppt, centrifuge the blue solution and discard the super. To the remaining test tube that may or may not appear to have a ppt, add a few drops of sodium stannite solution that has been freshly prepared. An immediate jet black color is positive for bismuth.

NOTE: to prepare sodium stannite solution, place one drop of tin chloride reagent in a test tube. Add 6M sodium hydroxide drop-by-drop with mixing until the ppt that is generated redissolves. You now have your sodium stannite solution.

⓿I Obtain a sample of known cations for this group and procure your unknown super (❷S 2) from the previous experiment for continuing your work through the qual cation analysis schemes. To both solutions, confirm the approximate hydrogen ion concentration (check against red litmus) as either acid or neutral.

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❶T Add 6M ammonia to the solutions a drop at a time until the litmus turns from red to blue. To your basic solutions, add 2M hydrochloric acid a drop at a time with mixing/stirring until the pH is between 2 and 3 (use wide-range pH paper). Add 0.35 mL (7 drops) of 2 M hydrochloric acid. To the now acidic (pH of about 0.5) mixture, add 4 gtts thioacetamide (TA) and enough distilled water to make a final volume of 2.5 mL. Place the mixtures in a boiling water bath for at least 5 minutes. Remove from the bath and centrifuge the tubes.

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❷T Separate the ppts and supers, combining as necessary to get them into one tube for the known ppt, one tube for the unknown ppt and one tube for the unknown super.

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❷S Set the combined unknown supers aside for future use (you don't need to keep the super from the known solution), sealed with Parafilm, labeled as "❷S 3" and stored as instructed.

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❸T Wash the ppts with 1 mL of hot distilled water that contains 1 gtt 6 M nitric acid and centrifuge. Add the washing from the unknown ppt to the super you obtained during this separation.

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❹T Pour the supers off into different tubes, confirm that the pH is not below 0.5 (if it is, raise it with the dilute ammonia), add 2 gtts TA and boil, again, for 5 minutes. Repeat no more than one more time, combining ppts and supers as before -- remember to save the unknown super, too as/with "❷S 3", above.

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❺T To each tube of ppt (known and unknown samples), add a half mL of 0.5M potassium hydroxide and heat for a few minutes in the boiling water bath. Centrifuge the tubes and dispose of the super – repeat the KOH washing of the ppt one more time, likewise disposing of the wash super. To these combined ppts, add 0.25 mL of water and 0.25 mL of 6M nitric acid and warm in the warm water bath – in this reaction, you're looking for bubbling (not boiling) to occur to float elemental sulfur and sulfides to the top of the reaction mixture. After 5 minutes, if no bubbles occur, centrifuge the samples, pouring off the super into another test tube – keep both super and ppt from this step.

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❻P To the ppts, add 6 gtts of Clorox and 2 gtts of 6M hydrochloric acid with stirring. Add 20 gtt water and heat to boiling. Now add 2 gtts tin chloride solution and centrifuge. **A white, grey or black ppt is positive for mercury.**

❻S Pour the supers into their own casseroles and add 2 gtts con sulfuric acid. Heat to evaporation over a micro-flame and under a ventilatory duct or siphon until copious amounts of white dense fumes are billowing out. Cool and carefully add 5 gtts distilled water and scrape with your glass stirring rod to loosen the solid from the walls of the casserole. Dump into a test tube, rinse casserole twice with distilled water and pour the rinsings into the test tubes, as well. Centrifuge and pour the super into a new test tube.

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❼P To the ppt, add a few drops of ammonium acetate solution with mixing. Centrifuge.

❼S To the super, add concentrated ammonia until the solution is alkaline to litmus. **A blue soln is positive for copper(II)**.

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❾S Even though you may not see a ppt, centrifuge the blue solution and discard the super.

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❽P Discard the remaining ppt.

❽S Add a drop of 6M HOAc and a few drops of potassium chromate to the resulting super. **A strong yellow ppt is positive for lead(II).**

⑩P To the remaining test tube that may or may not appear to have a ppt, add a few drops of sodium stannite solution that has been freshly prepared (see text for prep). **An immediate jet black color is positive for bismuth(II).**

Problem Set -- Cations: Hg (II), Cu (II), Pb (II) and Bi (II)

1. Draw a one page flow diagram showing what you did with Group II cations and your results.

2. Color the cations you separated in this group on the periodic table from the anion questions in a different color.

3. Is the difference between the solubilities of the hydroxide salts of Fe^{3+} and Mg^{2+} sufficient to permit the separation of Fe^{3+} and Mg^{2+} in a solution that is 0.1 M in each cation? If possible, what $[OH^-]$ is required to precipitate each cation?

4. Assuming that the dissociation of H_2S in H_2O follows the following reaction:

$$H_2S + 2H_2O = 2H_3O^+ + S^{2-}$$

and that the K for this reaction is:

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = 6.8 \times 10^{-23} = \text{"K"}$$

and that the $[H_2S]$ in aqueous solution is approximately 0.1 M,

What is the pH necessary to maintain the separation of Cd^{2+} and Tl^+ when precipitated as their sulfide salts? Assume the "10^{-5} rule" as minimum concentration. The solution is 0.1 M in each cation.

5. Given the following K_{sp}'s, determine the feasibility of separating the ion pairs as sulfide salts. Also determine the pH necessary to maintain the separation.

Salt	K_{sp}
CdS	3.6×10^{-29}
FeS	1×10^{-19}
La_2S_3	2×10^{-13}
MnS	5.6×10^{-16}
ZnS	1.1×10^{-21}

A: Fe^{2+} and Cd^{2+}
B: La^{3+} and Mn^{2+}
C: Cd^{2+} and Zn^{2+}

6. If a solution contains 0.005M CrO_4^{2-}, what concentration of Pb^{2+} must be exceeded by adding $Pb(NO_3)_2$ to the solution before $PbCrO_4$ will begin to precipitate (Neglect volume changes) ($K_{sp} = 1.8 \times 10^{-14}$).

7. A solution contains 0.005M KI and 0.05M KCl. $AgNO_3$ is gradually added. Which precipitates first: AgI or AgCl?

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