Chapter 16 – The Analysis of A Solution for Al (III), Ni (II), Zn (II), Fe (III) Ions	NAME:	
	Lab Section:	
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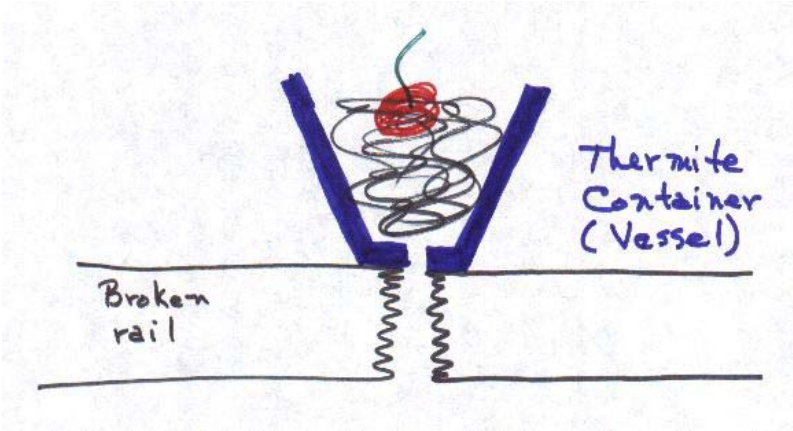
Introduction

Aluminum -- Al

Al has a silvery appearance, but dulls white due to oxidation. Weight for weight, it is twice as good a conductor of electricity as copper. It is resistant to corrosion. It is used in cooking utensils. Duralumin (Al, Cu, Mn, Mg) is very light and very strong and is used in aircraft. Aluminum bronzes (Cu with Si, Mn, Fe, Ni or Zn and Al) are around, too. Al has been used for crankcases and connecting rods in automobiles.

Thermite is a very interesting stuff and has several uses: rail welding and bombs in WW II. The rail welding is usually called the thermite reaction. The way it works is to have some guys drive up to a remote site on the railroad where a rail has broken; they hop out, place a container over the break and add the thermite mixture. They put a magnesium fuse in some ignition powder, light it and let 'er rip.



The reaction is $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$. In other words, the rail is welded in place at temperatures well above 3000°C. When used as bombs in WW II, they burned with high temperatures. Water doesn't quench this kind of fire, making them nasty armaments. A last use of Al is in Emery cloth -- the black cloth used to smooth rough ends on copper tubing or pipe. This is a combination of Al_2O_3 and Fe_3O_4 and is an excellent abrasive.

Nickel – Ni

Nickel is a silvery-white metal. It is hard, malleable and ductile. It is used in plating iron, steel and copper. Permalloy consists of Ni and Fe and is used in sound reproduction. Nichrome and Chromel consist of Ni, Cr, and Fe. Alnico consists of Al, Ni, Co and Fe. Platinite and Invar are used to "seal in" wires in light bulbs because they expand with the heat and maintain the vacuum in the light bulb; conversely, it shrinks with cooling

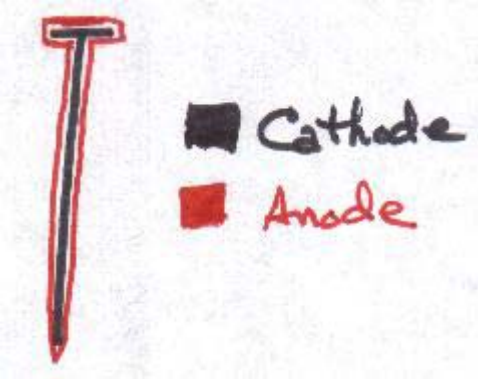
temperature and does the same thing (maintains vacuum) as the light bulb gets cooler. Ni powder is a hydrogenation catalyst of, among other things, unsaturated fatty acids.

Cobalt -- Co

Like Fe and Ni, Co is magnetic. Permanent magnets are made from Alnico (Al, Ni, Co and Fe), Hiperco (Co, Fe, Cr) and Vicalloy (Co, Fe, V). Cobalt is alloyed with iron and other metals for high speed cutting tools and surgical instruments. Black CoO gives glass a blue color. This glass is called cobalt glass. $CoCl_2 \bullet 6H_2O$ in alcohol is used as "invisible ink". To make it show up, heat the paper. As the salt dehydrates, the writing becomes blue. It fades upon rehydration from the environment.

Zinc -- Zn

Zn is a silvery metal that tarnishes to a blue-gray. It is used in dry cells, brass, bronze and used to coat iron. When it is used to coat iron or steel, it is called galvanization (making a battery). To make the nail not rust and, hence, make your fence fall apart, the nail (cathode) is coated with zinc (anode) to protect the nail from rusting (oxidation). ZnO is used for sunblock. Zn is hard and brittle at usual temperatures, but at 100-150°C is ductile and malleable -- this is when Zn ribbon is made.



Iron -- Fe

Iron pyrites are called fool's gold. It is an unsatisfactory iron source, although it is used as a sulfur source for sulfuric acid manufacture. Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) are used as iron ores. The metal formed from a blast surface is called pig iron.

Pig iron is brittle and is generally used to make cast iron. If it is re-melted and re-cooled, it forms cast iron. If pig iron is rapidly re-cooled, it forms Fe_3C, a white cast iron that is brittle, but hard and wears well. If the pig iron is re-cooled slowly, Fe_3C (gray cast iron; soft and tough) and graphite (C) are obtained.

Is it possible to obtain iron products that are both hard and wear well AND soft and tough for useful cast iron? YES! Cool the surface rapidly and the body of the casting slowly.

Steel consists of different alloys of iron. It's pig iron minus impurities plus some of the following: Mn, Cr, Ni, W, Mo, V and 0.04-2.5% C. There are three primary steels: Stainless steel (low carbon content and contains 12% or more Cr), Alloy steel (gives special properties for special uses; contains 1-5% Si for magnets) and Carbon steel (primarily iron and carbon). There are three Carbon steels:

Mild Carbon	Medium Carbon	High Carbon
This contains not more than 0.2% carbon and is ductile. It is used to make hot irons, wire and pipe. It usually contains 2-15% Si.	This steel contains 0.2-0.6% carbon. It's used to construct rails, structural steel and boilerplate. It usually contains about 10-18% Mn.	High carbon steel contains 0.6-1.5% carbon. It is hard to brittle. It is used to make surgical instruments, razor blades, springs and cutlery. It contains about 14-18% chromium and 7-9% nickel
These two steels can be forged and welded.		

Iron (III) tannate is nearly colorless. It is made by reacting tannic acid with ferrous sulfate. It is used as ink. When the salt is oxidized to ferric tannate, it turns black. Before that happens, though a dye makes the writing visible. You may have noticed how you thought you wrote something in blue, yet when you came back to it a day later it was black. You're right: the blue dye made the writing visible and then the black came through as the real ink was oxidized by the air. The ink can be cleaned off cloth by soaking it in ammonium oxalate for several hours. This treatment reduces the water insoluble ferric tannate to water-soluble ferrous tannate.

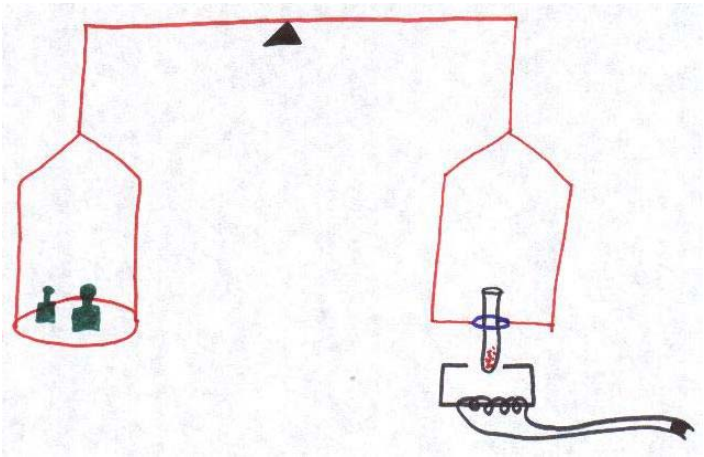
Iron salts were also used in blueprints. When ferric ammonium citrate is reacted with potassium ferricyanide, ferriferricyanide (bronze green) is formed. Blueprints are drawn on tracing cloth in black ink. When the blue print is made, the cloth is laid over the green blueprint paper. Hit it with light and the ferric ion is reduced to the ferrous ion, which leaves a blue precipitate wherever the light hits. Since the light doesn't go through the black lines, you're left with blue paper and white lines.

Iron metals need to be protected to reduce corrosion. They may be covered with paints, grease, asphalt, Zn (galvanized), Cu, Ni, Cr, Sn, Cd, Pb, ceramic enamel like you find on tubs or with adherent oxide (where the iron is treated superheated steam to form magnetic oxide: Fe_3O_4).

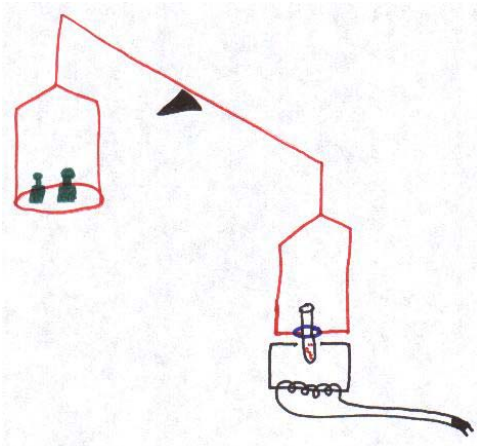
Iron, cobalt, nickel and gadolinium are all magnetic. There are three kinds of magnetism:

Paramagnetism	Diamagnetism	Ferromagnetism
In the case of paramagnetism, there are an odd number of unpaired electrons in the outer shell making the metal attract to a magnet.	In the case of diamagnetism, there is an even number of paired electrons in the outer shell, making the metal repel from a magnet.	Ferromagnetism is an extreme case of paramagnetism and leads to permanently magnetized magnets.

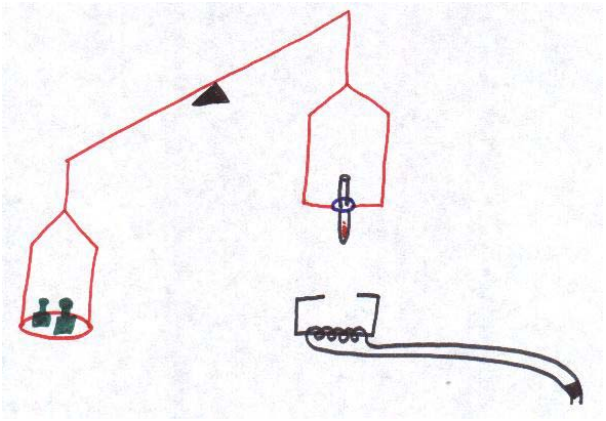
Paramagnetism is measured using a Guoy Balance. A Guoy Balance (Magnetic Susceptibility Balance is what they are using, now) is a balance on a knife-edge, right:



It has a pan on one arm and a test tube holder on the other that has an electromagnet associated with it. One places the sample in the test tube and adds masses to the pan to balance it out. The masses are recorded and the electromagnet turned on. If the sample is paramagnetic, **LEFT**, the sample is attracted to the electromagnet. Masses are added to re-balance it. The difference between the masses is used to calculate exactly how many unpaired electrons are in the outer shell.



If the sample is diamagnetic, **RIGHT**, the sample is repelled from the electromagnet. This has no practical use of which I am aware. The Magnetic Susceptibility Balance will be used in a future experiment in this course.



Experimental

Obtain a Group III Cation Known sample and your super from the previous experiment that you saved. As per previous experiments, a flow chart follows this narrative to clarify the verbage.

To both tubes, add dH_2O, qs 2 mL. To that solution, add 0.25 mL 6M ammonium chloride and alkalinize with con ammonia against litmus. Add an additional gtt in excess with mixing. Add 0.25 mL TA with stirring and boil for a minimum of 5 minutes. Spin and wash the ppt with hot dH_2O in which you put one crystal of ammonium nitrate. Combine the super with the washings. To the super and washings, add 20 drops con HCl and evap almost to dryness in a casserole. Add 1 mL dH_2O to casserole, pour the solution into a test tube, Parafilm ® it and label it ❷S4 and set it aside for later experiments.

To the ppt you obtained, above, add 20 gtts 6M hydrochloric acid with mixing (vortex, stirring rod or finger-flick). Pour mixture into a casserole and heat to a boil for about a minute over a micro-flame. Add 20 gtts distilled water with stirring and pour the mixture into a test tube. Centrifuge and separate the super from the ppt, label the super and hang onto it! Wash the ppt no more than two times with a mixture of 20 gtt 6M HCl and 20 gtt dH_2O each time, discarding the washings and keeping the ppt.

To the ppt, add 2 mL dilute aqua regia (1 mL 6M nitric acid and 1 mL 6M HCl) with stirring and place the tube in a boiling water bath for 2-3 minutes – the ppt ought to dissolve mostly, leaving a small residue – if visible, at all. Pour the resulting mixture into a casserole and boil carefully over a micro-flame for no more than 2 minutes. Add 20 gtts dH_2O and pour the solution back into the test tube. Centrifuge the sample, and pour the super off into another test tube. To the super, add several gtts of DMG (dimethylglyoxime). A rose-red ppt is positive for Ni(II).

To the super you obtained after adding the con HCl in the early stages of the analysis, add 20 gtts store-standard hydrogen peroxide (3% at Raleys). To this solution, add a drop at a time 6M NaOH until your solution is alkaline to litmus, then add 10 gtts in excess. Stir the solution then pour it into a casserole and boil carefully (with stirring) over a micro-flame for a couple of minutes. After boiling, pour the mixture into a test tube and centrifuge and separate the ppt from the super. Set the super aside for a few moments and focus on the ppt.

To the new ppt, add 20 gtts dH_2O and 20 gtts 6M sulfuric acid. Stir thoroughly (this may take several minutes) and centrifuge. To the super you obtain from this centrifugation, add 20-30 gtts dH_2O and a few drops of potassium thiocyanate. A deep red (almost blood red) color is positive for Fe(II).

Now go back to the super from the last sentence in the paragraph just before the previous one. Add 6M nitric acid until the solution is just acidic to litmus. Pour the

solution into a casserole and boil it down over a micro-flame until you have a final volume of about 2-3 mL. Pour the solution into a test tube and add 6M ammonia a drop at a time with mixing until the solution is alkaline to litmus. Even if you don't see a fine white gelatinous ppt in the mixture, centrifuge and pour the super into another tube and set aside.

To the just-obtained ppt, add 10 gtts 6M HNO_3 to dissolve the ppt. Spin and discard the residue. To the recovered super, add 20 gtts dH_2O and 2 gtts aluminon reagent with thorough mixing. Add 6M ammonia a drop at a time until the solution is alkaline to litmus. Spin – a red ppt is positive for Al(III) – the solution will be light pink to colorless.

Get out the last super from 2 paragraphs above (following the addition of the nitric acid and ammonia). Remove a sample from that tube via disposable pipet, and drop one drop of the super onto a piece of diphenylthiocarbazone paper. A purplish-red color is positive for Zn(II).

❶I Obtain a Group III Cation Known sample and your super from the previous experiment (❷S 3) that you saved.

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❶T To both tubes, add dH_2O, qs 2 mL. To that solution, add 0.25 mL 6M ammonium chloride and alkalinize with con ammonia against litmus. Add an additional gtt in excess with mixing. Add 0.25 mL TA with stirring and boil for a minimum of 5 minutes.

↓

❷P Spin and wash the ppt with hot dH_2O in which you put one crystal of ammonium nitrate.

→

❷S Combine the super with the washings. To the super and washings, add 20 drops con HCl and evap almost to dryness in a casserole. Add 1 mL dH_2O to casserole, pour the solution into a test tube, Parafilm ® it and label it "❷S 4" and set it aside for later experiments.

↓

❸P To the ppt, add 20 gtts 6M hydrochloric acid with mixing (vortex, stirring rod or finger-flick). Pour mixture into a casserole and heat to a boil for about a minute over a micro-flame. Add 20 gtts distilled water with stirring and pour the mixture into a test tube. Centrifuge and separate the super from the ppt.

↙ ↘

❹P Wash the ppt no more than two times with a mixture of 20 gtt 6M HCl and 20 gtt dH_2O each time, discarding the washings and keeping the ppt.

↓

❺P To the ppt, add 2 mL dilute aqua regia (1 mL 6M nitric acid and 1 mL 6M HCl) with stirring and place the tube in a boiling water bath for 2-3 minutes – the ppt ought to dissolve mostly, leaving a small residue – if visible, at all. Pour the resulting mixture into a casserole and boil carefully over a micro-flame for no more than 2 minutes. Add 20 gtts dH_2O and pour the solution back into the test tube. Centrifuge the sample, and pour the super off into another test tube.

❹S To the super, add 20 gtts store-standard hydrogen peroxide (3% at Raleys). To this solution, add a drop at a time 6M NaOH until your solution is alkaline to litmus, then add 10 gtts in excess. Stir the solution then pour it into a casserole and boil carefully (with stirring) over a micro-flame for a couple of minutes. After boiling, pour the mixture into a test tube and centrifuge and separate the ppt from the super. Set the super aside for a few moments and focus on the ppt.

<table>
<tr><td>↓</td><td colspan="2">↓</td></tr>
<tr><td>❺S To the second of the split samples, add several gtts of DMG (dimethylglyoxime). A rose-red ppt is positive for Ni(II).</td><td>❻P To the ppt, add 20 gtts dH_2O and 20 gtts 6M sulfuric acid. Stir thoroughly (this may take several minutes) and centrifuge. To the super you obtain from this centrifugation, add 20-30 gtts dH_2O and a few drops of potassium thiocyanate. A deep red (almost blood red) color is positive for Fe(II).</td><td>❻S Add 6M nitric acid to the super until the solution is just acidic to litmus. Pour the solution into a casserole and boil it down over a micro-flame until you have a final volume of about 2-3 mL. Pour the solution into a test tube and add 6M ammonia a drop at a time with mixing until the solution is alkaline to litmus. Even if you don't see a fine white gelatinous ppt in the mixture, centrifuge and pour the super into another tube and set aside.</td></tr>
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<tr><td>❼P To the ppt (that you may or may not see), add 10 gtts 6M HNO_3 to dissolve the ppt. Spin and discard the residue.</td><td>❼S Remove a sample of super from that tube via disposable pipet, and drop one drop of the super onto a piece of diphenylthio-carbazone paper. A purplish-red color is positive for Zn(II).</td></tr>
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<tr><td colspan="3">❽S Add 20 gtts dH_2O and 2 gtts aluminon reagent to the super with thorough mixing. Add 6M ammonia a drop at a time until the solution is alkaline to litmus. Spin – a red ppt is positive for Al(III) – the solution will be light pink to colorless.</td></tr>
</table>

Problem Set: Al (III), Ni (II), Zn (II), Fe (III)

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

2. Color in the squares in the periodic table you used in the Anions problem set for the cations in this experiment.

Compound	K_{sp}
$Al(OH)_3$	1.4×10^{-34}
$Cd(OH)_2$	2.8×10^{-14}
$Cr(OH)_3$	7×10^{-31}
$Co(OH)_2$	2×10^{-16}
$Cu(OH)_2$	2.2×10^{-20}
$Fe(OH)_3$	6×10^{-38}
$Pb(OH)_2$	4×10^{-15}
$Mg(OH)_2$	1.1×10^{-11}

Use the above table of K_{sp} values for the following 3 questions.

3. What pH is necessary to separate Al^{3+} from Cd^{2+} as hydroxide salts if both cations are present at 0.1 M. Also use the 10^{-5} rule.

4. Determine the same information with the same cation concentrations for Pb^{2+} and Cd^{2+}.

5. Perform the same operations for Al^{3+} and Fe^{3+}.

6. Determine a simple and quick method to determine if your ring is pure silver or sterling silver (copper-silver).

7. Design a simple and quick method to determine if the black lump at a campsite in Big Meadows is charcoal or pyrolusite (MnO_2).

8. Design a simple and quick method to determine if the brazing rod is copper and zinc or silver and zinc.

9. Design a simple and quick method to determine if the "silver" stone you found in Virginia City is pure silver or galena (PbS).

10. Design a simple and quick method to determine if the yellow flakes in the boulder next to Ophir Creek is gold or iron pyrites (Fe_xS_y).

11. Design a simple and quick method to determine if the tiny, odd-shaped, pebble on Carson Street outside the Nugget is a pebble of galena (PbS) or someone's filling (silver-mercury amalgam) knocked out of a tooth over a hand of poker.

12. Design a simple and quick method to determine if the red scum on the rocks next to the Carson River is cinnabar (HgS) or bauxite (Al ore).

13. Design a simple and quick method by which to determine if the white solid found in an old mine shack is useful (calomel; Hg_2Cl_2) or poisonous (corrosive sublimate; $HgCl_2$).

14. Write the chemistry for the formation of copper (II) sulfide from thioacetamide.

15. Will lead sulfate precipitate if 100 mL 0.001M lead nitrate solution is added to 100 mL 0.002M magnesium sulfate.

16. Will lead chloride precipitate if 50 mL 0.1M lead nitrate are mixed with 20 mL 0.04M sodium chloride?

17. Will silver acetate form if 18 mL 0.1M silver nitrate are mixed with 40 mL 0.02M sodium acetate? $K_{sp} = 4 \times 10^{-4}$ for AgOAc.

18. In a saturated solution of MgF_2 in water, $[Mg^{2+}] = 2.7 \times 10^{-3}$M. What is the K_{sp} for MgF_2?

19. Write your own qualitative analysis question and answer it.

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