Experiment 8: Separation Of Cations

(Qualitative Analysis)

This experiment has a four-fold purpose:

1. To show you how differing chemical properties of cations may be used to effect their separation and identification.
2. To teach you a little descriptive chemistry.
3. To help you make careful observations.
4. To interpret the data you have obtained which will enable you to devise your own scheme of separation and identification for a group of cations.

In this experiment you will determine which metals are in an unknown solution. In order to solve this question, you will first perform a series of reactions with known cations to observe and determine how they can be separated from each other. Given this information you will develop a flow chart illustrating the method in which you plan to separate the cations of the unknown mixture. The flow chart will be based upon the results of the reactions you observed while testing the known cations.

On the second day you will receive an unknown that will consist of a mixture of one to four cations. Your job will be to isolate each cation and run a confirmation test on it to prove its presence (or absence).

An Example

Consider the observations recorded by a student when examining the cations Al^{3+}, Zn^{2+}, and Mn^{2+}: The student began by entering the three cations in the top row of a grid sheet and the reagents, 6.0 M HCl, 0.1 M NaOH, 6.0 M NaOH, 0.1 M NH_3, and 6.0 M NH_3 in the left column next to the margin. To three labeled test tubes she added 1 mL of each metal cation solution followed by addition of 6.0 M HCl. To three other test tubes she added the cation followed by **<u>CAREFUL</u>** (with the aid of an eye dropper) dilute NaOH. Once (or if) precipitation occurred with the dilute reagent, the concentrated reagent was used to see if the precipitate dissolved. If a precipitate was formed with NH_3 or NaOH, the mixture was centrifuged, the supernatant removed, and nitric acid was added to the solid. This part was not put in the Example below.

reagent ¯	Al^{3+}	Zn^{2+}	Mn^{2+}
6.0 M HCl	NOR	NOR	NOR
0.1 M NaOH	wht. gel. ppt.	wht. ppt.;	wht. ppt.
6.0 M NaOH	dis. x's base	dis. x's base	ppt. remains
0.1 M NH_3	wht. gel. ppt.	wht. ppt.	wht. ppt.
6.0 M NH_3	ppt. remains	dis. x's base	ppt. remains

The Formation of Complex Ions (Continuation of the Example)

A ligand is a molecule or ion that has a lone pair of electrons that can be used to form a coordinate covalent bond to a metal ion. A complex ion consists of a metal ion surrounded by a number of ligands such as OH^-, NH_3, and CN^-. Complex ions are soluble substances $_{(aq)}$ formed by the addition of excess (x's) reagent to the initial precipitate formed. You are asked to write net-ionic equations for <u>all</u> of the observed reactions. This is illustrated using the information from the grid above:

$$Al^{3+}_{(aq)} + 3\ OH^-_{(aq)} \rightarrow Al(OH)_{3(s)}$$ **wht. gel. ppt.**

$$Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)}$$ **dis. x's base**

This scheme indicates that addition of strong base to aluminum ion results in the formation of a precipitate; addition of more (x's) base results in the formation of the soluble tetrahydroxoaluminate ion.

The **molecular equation** would read: $Al(NO_3)_{3(aq)} + 3\ NaOH_{(aq)} \rightarrow Al(OH)_{3(s)} + 3\ NaNO_{3(aq)}$

The **complete ionic equation** would be:

$$Al^{3+}_{(aq)} + 3\ NO_3^-{}_{(aq)} + 3\ Na^+_{(aq)} + 3\ OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} + 3\ Na^+_{(aq)} + 3\ NO_3^-{}_{(aq)}$$

The **net ionic equation** is: $Al^{3+}_{(aq)} + 3\ OH^-_{(aq)} \rightarrow Al(OH)_{3(s)}$

The other **molecular equation** is: $Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)} + Na^+_{(aq)}$

The **complete ionic equation** is: $Al(OH)_{3(s)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)} + Na^+_{(aq)}$

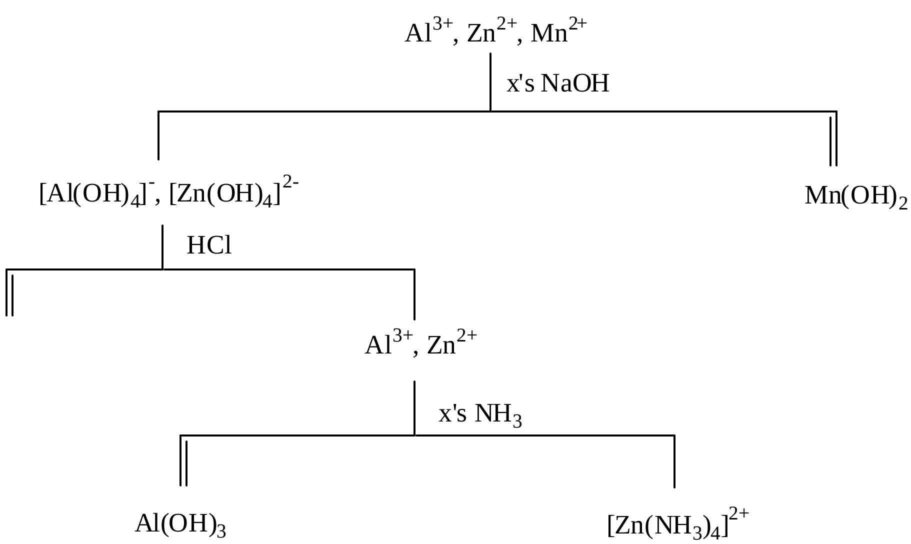
The other **net ionic equation** is: $Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)}$

Also, recall that all "insoluble" bases dissolve (go into solution) in strong acid liberating the metal ion.

$$Al(OH)_{3(s)} + 3\ H^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3\ H_2O_{(l)}$$

Obviously, if you add NH_3 - a neutral molecule - to a cation, you should only be able to attain a cationic species that would be soluble. However, precipitate formation is often observed upon addition of ammonia. The precipitate will often subsequently dissolve upon the addition of x's ammonia.

After conducting the procedures shown in Sections II and III, you will be required to construct a flow chart that shows systematically how you will experimentally proceed to analyze an unknown solution. The data shown in part II may be arranged in the form of a flow chart after applying some thought as follows:



You should note that the vertical double lines have solids below them and that the single vertical lines always have aqueous solutions (ionic species) below them.

Your flow chart may not necessarily begin with NaOH addition to the metal cations! It may begin with HCl, dilute NaOH or NH_3, or concentrated NaOH or NH_3. When writing your flow chart, pay attention to what products are formed at each step and include them in your diagram. For example, when the cations are reacted with x's NaOH, the precipitate $Mn(OH)_2$ is formed along with 2 complex ions.

Preliminary Test Procedure - Week 1
You will be given five test solutions each one containing one of the cations to be investigated, i.e., Ag^{+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Fe^{3+}. Reread part II and prepare a grid as shown.

Write net ionic equations for any chemical reaction that occurred knowing that the complex ions you may encounter in this experiment are:

$[Cu(NH_3)_4]^{2+}$ $[Ag(NH_3)_2]^{1+}$ $[Ni(NH_3)_6]^{2+}$ $[Cr(OH)_4]^{-}$.

Following this, diagram a flow chart.

Confirmation Tests – Weeks 1 and 2
From the example at the beginning of the lab, one could presume the white precipitate formed when ammonia is added to the Al^{3+} and Zn^{2+} mixture is aluminum hydroxide and that the colorless solution contains the zinc complex. Not good enough. You must make additional tests to clearly establish the presence or absence of aluminum and zinc in your unknown. These are called confirmation tests and are used to conclusively state whether or not a cation is present. Typically these work best when the cation has already been isolated. The confirmation tests should not be performed on mixtures of cations! Examples of confirmation tests for the cations in the Example are as follows:

These are as follows:

1. $Al(OH)_{3(s)} + HNO_3 \rightarrow Al^{3+}$ + aluminom (red dye) + $NH_3 \rightarrow Al(OH)_3$ (red lake-doesn't sink)
Presence of a red lake confirms the presence of aluminum.

2. $[Zn(NH_3)_4]^{2+}{}_{(aq)} + HCl \rightarrow Zn^{2+} + K_4[Fe(CN)_6] \rightarrow K_2Zn[Fe(CN)_6]_2$ (light gr. ppt.)
Presence of a light green precipitate confirms the presence of zinc.

3. $Mn(OH)_{2(s)} + H_2SO_4 \rightarrow Mn^{2+} + HNO_3 + NaBiO_3 \rightarrow MnO_4^{-}$ (pink)
Presence of a pink colored solution confirms presence of manganese.

The confirmation tests for your five possible metals are below. Make sure they work as described.

1. Silver. To the white solid (AgCl) add 6.0 M NH_3. After the precipitate dissolves, add 6.0 M HNO_3; appearance of a white precipitate shows the presence of silver.

2. Chromium. To the dark green basic $Cr(OH)_4^{-}$, add 3% H_2O_2 until you see the deep yellow CrO_4^{2-}. Add Ba^{2+} to yield the yellow precipitate $BaCrO_4$. <u>Redissolve</u> the precipitate with 6 M HNO_3 and add several drops of H_2O_2. A blue color appears which may fade rapidly.

3. Nickel. Return the nickel to the +2 state using 3.0 M HCl. Add sufficient 6.0 M NH_3 in order to obtain a deep-blue solution. Adjust pH to 8 using NH_3 and HCl and then add several drops of dimethylglyoxime (DMG) solution. Obtain red lake of $Ni(DMG)_2$.

4. Iron. Return the iron to the +3 state using 6.0 M HCl. Add several drops of 0.10 M KSCN. Solution turns deep red due to formation of $[FeSCN]^{2+}$.

5. Copper. To the blue $[Cu(NH_3)_4]^{2+}$ solution, add 6.0 M acetic acid until the color fades. Add

several drops of 0.10 M $K_4[Fe(CN)_6]$, which forms a red-brown precipitate of $Cu_2[Fe(CN)_6]$.

Test your Flow Chart

Given that you will not have Cu^{2+} and Ni^{2+} together in your unknown solution, does your flow chart work? If not, fine-tune it. Do the confirmation tests work on these "isolated" ions as well?

Unknowns - Week 2

You will be given an unknown which will contain anywhere from 0 to 4 cations. You must determine those that you do and don't have. Therefore your grade will depend in every way on all of the results you have obtained during these three weeks.