

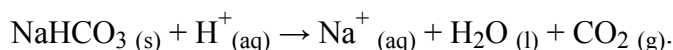
## Experiment 2: The Qual Scheme Cation Group I

### Note About Notation:

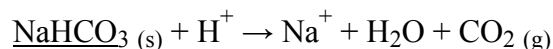
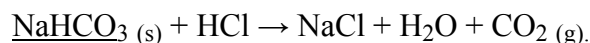
When describing chemical reactions by writing chemical formulas and chemical equations, it is important to balance the equations (with respect to charge and mass) and to specify the physical state (solid (s), liquid (l), gas (g), or dissolved in water (aq)) of each chemical species (elements, molecules, salts, or ions). For example,



or alternately written in ionic form as

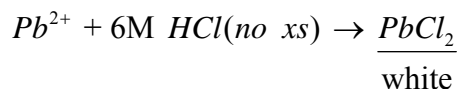
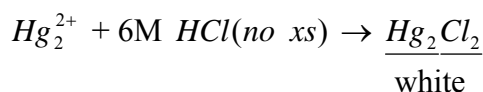
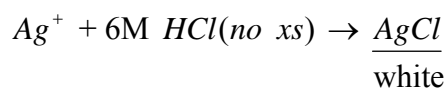


For the qualitative analysis experiments in this manual (Experiments 2, 3, and 4), it is understood that most species (all ions) are in aqueous solution. For these solute species, no physical state notation is used. To indicate a solid species (like a precipitate), the formula is underlined. Thus the previous equation might be written as follows:

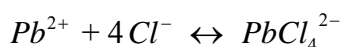


### Group I Reactions

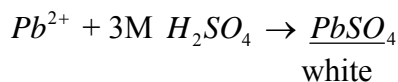
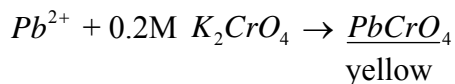
You will note from the solubility rules that three cations, ( $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$ ), those having insoluble chloride salts, are easily separated from all others.



Silver and mercurous chlorides are very insoluble in water and are not greatly affected by excess chloride. Lead chloride, however, is much more soluble in water and also forms a soluble complex ion

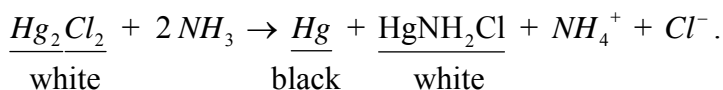


Therefore in Proc 1 we try to keep the excess chloride ion concentration low. In Proc 2 we take advantage of the relative large solubility of  $PbCl_2$  and its favorable temperature coefficient to separate  $PbCl_2$  from  $AgCl$  and  $Hg_2Cl_2$  which we have no chance of dissolving in mere hot water. In Proc 3 final testing for lead involves two separate reactions which each form a precipitate.

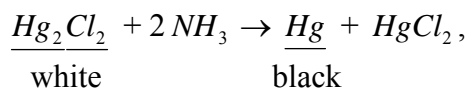


Since  $K_2CrO_4$  solution is vivid yellow the color of the test solution will be yellow even without the presence of lead: there must be a precipitate for a positive lead test. Note here, as with most of the qual scheme, many cations form yellow insoluble salts with chromate and some form white precipitates with sulfate; therefore, the separation done in Procs 1 & 2 must precede Proc 3.

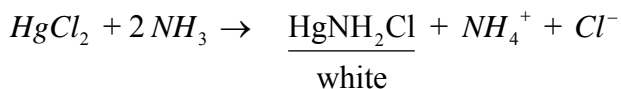
The second application of hot water to the precipitate from Proc 1 is necessary to dissolve all the  $PbCl_2$  which will otherwise confuse your decision about the presence of silver. In Proc 4 concentrated ammonia (aq) [sometimes called ammonium hydroxide (See endnote of this experiment)] is added directly to the white precipitate from Proc 2. If  $Hg_2Cl_2$  is present the following overall reaction will occur.



This involves the disproportionation of  $Hg_2Cl_2$  in base,

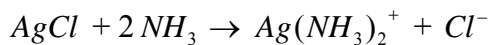


followed by precipitation of the salt of an unusual anion  $NH_2^-$  (amide)

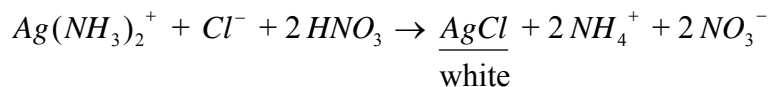


In any case, the distinct behavior of white precipitate turning black (or dark grey) identifies the presence of  $Hg_2^{2+}$  in the original solution.

If  $AgCl$  is present in the precipitate from Proc 2 it will dissolve on addition of 15M  $NH_3$



so that the decantate after the addition of 15M  $NH_3$  should contain any silver as a complex cation. When this decantate is made acidic by 16M  $HNO_3$  the complex is disrupted and  $AgCl$  reprecipitates

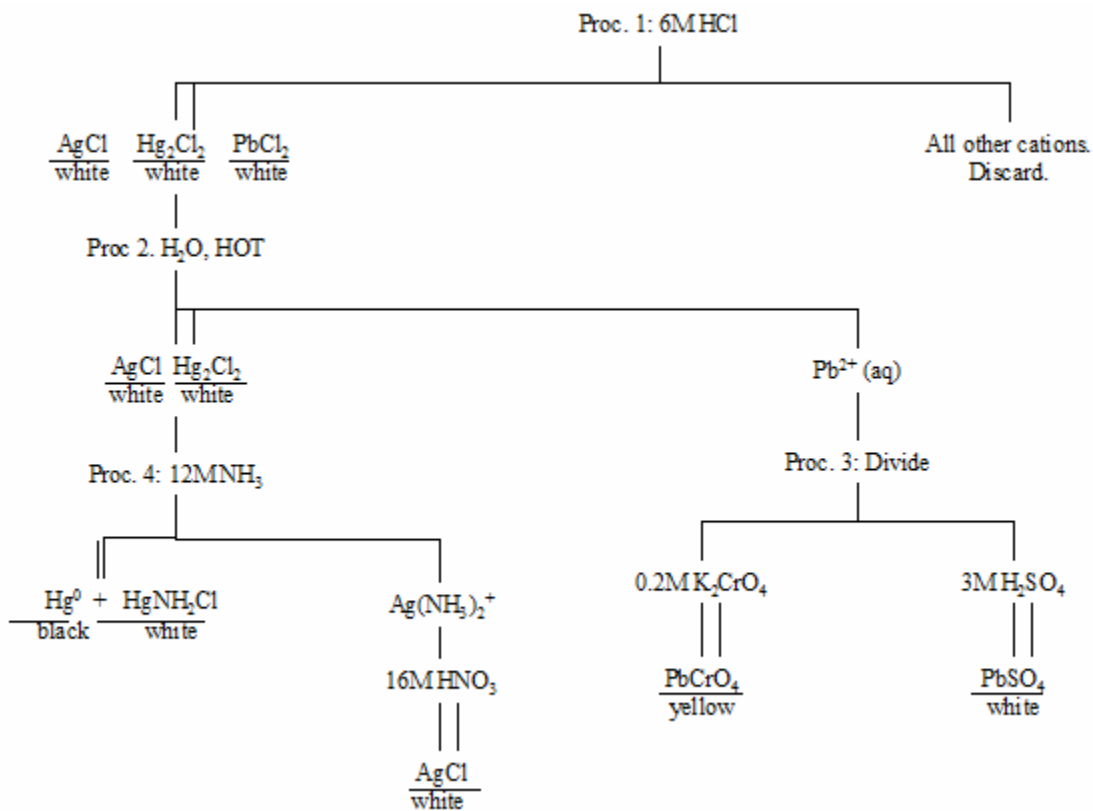
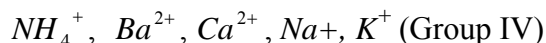
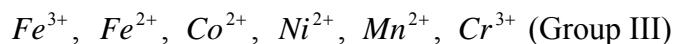
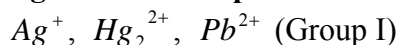


## Group I Procedures

### Procedure 1

Take about 6 drops of the “solution to be analyzed” in a test tube and dilute it with an equal volume of water. Add 3 drops of 6M HCl and mix. If a precipitate appears indicating the presence of one or more Group I ions, centrifuge. “Test for completeness of precipitation” by adding a single drop of 6M HCl, letting it run down the side, and examine for cloudiness where the solutions mix. When you are satisfied that precipitation is complete decant the supernatant. Since analysis of Group II, etc., will not be done, the decantate may be discarded. “Wash” the precipitate with 6 drops of water (discard wash) and take the precipitate to Proc 2.

### Flow Diagram for Group I: Procedures 1-4



### ***Procedure 2***

Put 20 drops of water in with the precipitate from Proc 1 and place the tube in your boiling water bath, stirring for 1 min. The next operations should be carried out quickly. Get a balance tube ready and spot an available centrifuge before taking the sample out of hot water. Then quickly spin about 30 sec. and decant quickly to minimize cooling. The decantate will contain most of the  $\text{PbCl}_2$  if present. Test it according to Proc 3. Wash the remaining precipitate with 10 drops of hot water (in the same manner) but discard the wash. Save the precipitate for analysis according to Proc 4.

### ***Procedure 3***

Divide the decantate from Proc 2 into two equal parts.

To one part add 2 drops of 0.2M  $\text{K}_2\text{CrO}_4$ . If  $\text{Pb}^{2+}$  is present a yellow precipitate is produced. To the other part add 2 drops of 3M  $\text{H}_2\text{SO}_4$ , a white precipitate will form if  $\text{Pb}^{2+}$  is present in solution. The chromate test is more sensitive, there must be precipitate, significant cloudiness at the least.

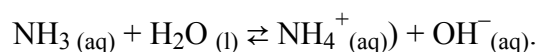
### ***Procedure 4***

Add 5 drops of 15M  $\text{NH}_3$  (hood) to the washed white precipitate from Proc 2. Immediate conversion of the precipitate to dark grey or black indicates the presence of mercurous ion,  $\text{Hg}_2^{2+}$ . If at this stage some white cloudiness persists, it usually is  $\text{PbCl}_2$ , which was not washed out in Proc 2 and will require a little extra centrifugation. Centrifuge and separate the clear decantate.

Take the decantate to the hood and add 16M  $\text{HNO}_3$  dropwise (a very vigorous reaction) until a white precipitate appears or until the solution is acid to litmus. The white precipitate is  $\text{AgCl}$ , appearing as the ammonia complex is decomposed by acid, and proves the presence of  $\text{Ag}^+$ .

### **Endnote:**

When an aqueous solution is created which contains ammonia ( $\text{NH}_3$  (aq)) molecules, ammonium cations ( $\text{NH}_4^+$  (aq)), and hydroxide anions ( $\text{OH}^-$  (aq)), the following equilibrium is established.



This equilibrium is strongly shifted to the left. Thus, regardless of how the solution was prepared, ammonia is by far the major component (other than water). Hence the solution should be labeled as aqueous ammonia, rather than as aqueous ammonium hydroxide. You will find that under the hood, it is erroneously labeled as 15M ammonium hydroxide. Don't be confused if the lab manual calls for 15M ammonia.