5 Complex Ion Equilibria

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- **Observe the properties of some complex ions in water solution.**
- **Apply equilibrium concepts to complex ions.**
- **Use the centrifuge as a tool in separating and identifying ions in solution.**

DISCUSSION

A complex ion is an electrically charged molecule made of two parts, a *central atom* (usually a metal ion) and one or more ligands. Ligands are molecules or ions, containing lone electron pairs, that are covalently bonded to the central atom. Both electrons in the bond come from the ligand. A bond of this type is called a coordinate covalent bond, and compounds formed in this way are often called coordination compounds. Coordination compounds usually contain one or more complex ions.

The charge on a complex ion is determined by the charge on the central atom and the charges on the ligands. The +2 charge on $Ca(H_2O)_6^{2+}$, for example, comes from the central atom (the calcium ion) since the ligands (water molecules) are neutral. The -3 charge on $Ag(S_2O_3)_2^{3-}$ is the sum of the +1 charge on the silver ion and the -2 charge on each of the thiosulfate ligands. As you do this experiment and write formulas for complex ions, take care to show the correct charges.

Metal ions in neutral or acidic solution are actually complex ions, water being the ligand. For example, the calcium ion in water is more accurately represented by the formula $Ca(H_2O)_6^{2+}$ than by Ca^{2+}. Other metals are similar, although the number of water molecules bonded to the metal ion varies. For simplicity, however, symbols such as $Ca^{2+}$and Al^{3+} are usually written.

When a base is added to a solution containing metal ions, most metals precipitate as the hydroxides. Examples are Al^{3+}, which forms $Al(OH)_3$*(s)*, and Fe^{3+}, which forms $Fe(OH)_3$*(s)*. Addition of acid dissolves the precipitate, forming the metal ion again. Some metal hydroxides will also dissolve when excess strong base is added because of the formation of complex ions in which OH^- is the ligand. $Al(OH)_3$, for example, not only dissolves in acid to form Al^{3+}, but also dissolves in excess NaOH to form $Al(OH)_4^-$. Such hydroxides are called amphoteric hydroxides**.**

There are also many hydroxides that dissolve in excess ammonia. In these cases NH_3 is usually the ligand since there is much more NH_3 in solution than OH^- in a solution of this weak base.

The table below summarizes the behavior of several metal ions in solution. Water as a ligand has been omitted. Notice that some hydroxides

Acidic or Neutral	Slightly Basic	Excess NaOH	Excess NH_3
Al^{3+}	$Al(OH)_3$*(s)*	$Al(OH)_4^-$	$Al(OH)_3$*(s)*
Ni^{2+}	$Ni(OH)_2$*(s)*	$Ni(OH)_2$*(s)*	$Ni(NH_3)_6^{2+}$
Fe^{3+}	$Fe(OH)_3$*(s)*	$Fe(OH)_3$*(s)*	$Fe(OH)_3$*(s)*
Cr^{3+}	$Cr(OH)_3$*(s)*	$Cr(OH)_4^-$	$Cr(OH)_3$*(s)*
Cu^{2+}	$Cu(OH)_2$*(s)*	$Cu(OH)_2$*(s)*	$Cu(NH_3)_4^{2+}$

dissolve in excess NaOH*(aq)*, and some dissolve in excess NH_3*(aq)*. (There are even some that dissolve in both). Be aware that silver forms the complex ion $Ag(NH_3)_2^+$.

Finally, you will see some other examples of interesting and colorful complex ions and coordination compounds, some of which are used to identify metal ions in solution. You will also gain experience in using a centrifuge to separate precipitates from solutions.

PROCEDURE

**Complex Ions in
Sodium Hydroxide and Ammonia**

1. Into ten small test tubes, place 2 mL samples of 0.1 *M* solutions of Al^{3+}, Ni^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ag^{+}, Pb^{2+}, and Zn^{2+}. Use nitrates or chlorides. Note the color of each metal ion (remember each is a complex ion with water as the ligand), and record it in the first column of the table on the report.

2. To each of these solutions add 1 drop of 6 *M* NaOH*(aq)*. If no precipitate forms, add more NaOH, a drop at a time, until it does. Mix well, and use the centrifuge if necessary to speed the settling of the precipitates. (Your instructor will tell you how to use the centrifuge.) Write the formula and record the color of each of the hydroxide precipitates in the second column (Ag_2O is formed instead of AgOH).

3. Then add 1 mL of 6 *M* NaOH*(aq)* to each test tube and stir well with a stirring rod. Add more NaOH if needed until four of the precipitates dissolve. The complex ions formed have four hydroxide ligands except for lead, which has three. Write the formula and record the color of each complex ion in the third column.

4. Which of the hydroxide precipitates are amphoteric? List the amphoteric hydroxides.

5. Write the net ionic equations for the reaction between Zn^{2+} and the first drop of 6 *M* NaOH*(aq)*. According to LeChatelier's Principle, which direction should the reaction shift when you add more NaOH solution to the test tube? Indicate the direction with an arrow.

6. Write the net ionic equation for the reaction that actually occurred when you added excess NaOH solution to the test tube.

7. To the solution containing the zinc complex ion, add 6 *M* HCl*(aq),* a drop at a time with stirring, until a precipitate forms, then keep adding HCl solution until it redissolves. Write net ionic equations for these two reactions.

8. Add 2 mL of 6 *M* NH_3*(aq)* to ten new solutions of the metal ions. Stir them well. The precipitates that form are the same as those formed with NaOH. Notice, however, that several of the precipitates that first form will dissolve with stirring. (One will dissolve partially, producing a colored solution). Record the colors of the complex ions and write their formulas in the fourth column of the table on the report. (Three of the formulas are found in the discussion section. The cobalt complex has six NH_3 ligands). The zinc complex has four ligands, but is its formula $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$? Zinc is the only one that dissolves in both NaOH and NH_3, and in Steps 9-12 you will discover the formula of the complex ion. Save the test tube containing silver for Step 13.

9. To a 10 mL sample of 0.1 *M* Zn^{2+} in a small beaker, add 6 *M* NaOH*(aq),* one drop at a time with mixing, until the hydroxide precipitate just dissolves. Measure the pH of the solution with some pH paper, and calculate $[OH^-]$.

10. Now repeat, using 6 *M* NH_3*(aq)* until the precipitate just dissolves. Again measure the pH of the solution, and calculate $[OH^-]$.

11. Is there sufficient OH^- in the ammonia solution to form $Zn(OH)_4^{2-}$? Decide whether the complex ion with ammonia is $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$.

12. Write the net ionic equation for its formation from the hydroxide precipitate. Also, fill in the correct formula in the table on the report.

Other Complex Ions of Interest

13. To the test tube from Step 8 containing the diamminesilver complex ion, add a few drops of 0.1 *M* KBr*(aq)*. The off-white precipitate, AgBr*(s)*, is the light-sensitive compound most often used in photographic film. Now add enough 1 *M* $Na_2S_2O_3$*(aq)* to dissolve the precipitate. This is the reaction used when developed film is placed in fixer solution. The complex formed is $Ag(S_2O_3)_2^{3-}$. Write net ionic equations for the reactions.

14. In a small test tube, combine 2 mL of 0.1 *M* $Fe(NO_3)_3$*(aq)* with 2 mL of 0.1 *M* KSCN*(aq)*. The deeply colored complex, $Fe(SCN)_6^{3-}$, is evidence for the presence of iron in a sample. Describe its appearance.

15. In a small test tube combine 2 mL of 0.1 *M* $Ni(NO_3)_2$*(aq)* with a few drops of dimethylglyoxime solution. The precipitate, an insoluble coordination compound, is evidence for the presence of nickel. Describe its appearance.

Separation of Metal Ions

16. Combine 2 mL of 0.1 *M* $Fe(NO_3)_3$*(aq)* with 2 mL of 0.1 *M* $Ni(NO_3)_2$*(aq)*. Add 2 mL of 6 *M* NH_3*(aq)* and mix well. Centrifuge the test tube, and save the precipitate for Step 18. Write the net ionic equations for the two reactions occurring when NH_3 is added to a mixture of Fe^{3+} and Ni^{2+}.

17. Divide the solution between two test tubes. In one, test for iron by adding a little 0.1 *M* KSCN*(aq)* as in Step 14. Test for nickel by adding a little dimethylglyoxime solution to

the other. Record your observations and conclusions.

18. Wash the precipitate you saved from Step 16 by adding 2 mL water, mixing well, centrifuging, and discarding the water. Dissolve the precipitate in a few drops of 6 *M* HCl*(aq)* and add 2 mL of water. Divide this solution and test one portion for iron, the other portion for nickel. How well have you separated the two metal ions?

19. Based on your results from Steps 1-3, find two ways of separating chromium and copper ions. One approach would be to precipitate the copper while leaving the chromium in solution. The other would be to precipitate the chromium while leaving the copper in solution. Try these out on a mixture of the two. After separating them, make the solutions acidic (or dissolve the precipitates) with HNO_3*(aq)* or HCl*(aq)*, and compare the colors with the original solutions. Write net ionic equations for the two separation methods.

5 Complex Ion Equilibria

Name ______________________________
Section __________________Locker ____
Instructor ___________________________

Enter the data or answer the questions according to the corresponding step in the procedure.

Complex Ions in Sodium Hydroxide and Ammonia

1-3. Based on your observations, record the colors of the metal ions, precipitates, and complex ions in the spaces below. Also write the formulas for the precipitates and complex ions. In the last two columns, leave the spaces blank if the precipitates do not dissolve.

Metal ion ion	**Color**	**Precipitate:** Formula and color	**Complex** With 1 mL NaOH*(aq)*: Formula and color	**Complex** With 2 mL NH_3*(aq)*: Formula and color
Al^{3+}				
Ni^{2+}				
Fe^{3+}				
Cr^{3+}				
Cu^{2+}				
Mn^{2+}				
Co^{2+}				
Ag^{+}				
Pb^{2+}				
Zn^{2+}				

4. Which of the hydroxide precipitates are amphoteric?

5. Write the net ionic equation for the reaction between Zn^{2+} and the first drop of 6 *M* NaOH*(aq)*. According to LeChatelier's Principle, which direction should the reaction shift when you add more NaOH*(aq)* to the test tube? Indicate the direction with an arrow.

6. Write the net ionic equation for the reaction that actually occurred when you added excess NaOH*(aq)* to the test tube.

7. Write the net ionic equations for the two successive reactions that occurred when HCl*(aq)* was added.

8. Record your observations (of adding ammonia to the metal ions) in the table on the first page.

9-10. Record the pH and $[OH^-]$ of Zn^{2+} solutions after addition of $NaOH$*(aq)* and NH_3*(aq)*:

	pH	**[OH]**
Zn^{2+} + $NaOH$*(aq)*		
Zn^{2+} + NH_3*(aq)*		

11. Is there sufficient OH^- in the ammonia solution to form $Zn(OH)_4^{2-}$? Is the complex ion with ammonia $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$

12. Write the net ionic equation for its formation from the hydroxide precipitate. Also, fill in the correct formula in the table on the first page.

Other Complex Ions of Interest

13. Write the net ionic equations for the reactions occurring when, first, potassium bromide, then sodium thiosulfate, are added to the solution containing the diamminesilver complex ion.

14. Describe the appearance of the complex ion formed in the test for the presence of iron.

15. Describe the appearance of the coordination compound formed in the test for the presence of nickel.

Separation of Metal Ions

16. Write the net ionic equations for the two reactions occurring when NH_3*(aq)* is added to a mixture of Fe^{3+} and Ni^{2+}.

17. Describe what happened when you tested the <u>solution</u> for Fe^{3+} and Ni^{2+}. What do you conclude?

18. Describe what happened when you tested the precipitate for Fe^{3+} and Ni^{2+}. What do you conclude? How well were the two ions separated?

19. What reagent did you add to precipitate the copper but leave the chromium in solution? Describe the result when you added this reagent to a mixture of chromium and copper ions.