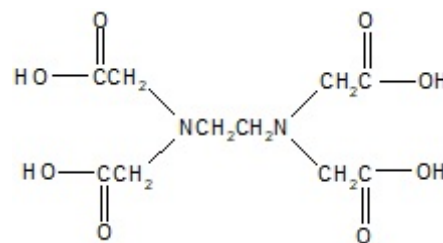Experiment 1 (see http://murov.info/chemexpts.htm
for additional experiments)
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# COMPLEXES

ethylenediaminetetraacetic acid (EDTA)

## Learning Objectives

Upon completion of this experiment, students will have experienced:
1.  The qualitative observation of complexes.
2.  Calculations involving equilibrium constants for complex formation, acid dissociation and solubility.
3.  The analysis of cations using precipitation reactions.

## Text Topics

Complexes, solubility products, formation constants for complexes, qualitative analysis schemes.

## Notes to Students and Instructor

This experiment should be studied and some calculations and predictions made before the laboratory period begins.  It is helpful for these predictions if Part A is performed the first week and Parts B and C the second week.

## Discussion

The melting point of sodium chloride is 801°C.  The crystalline array with each sodium surrounded by 6 chlorides and each chloride surrounded by 6 sodium ions must have very strong attractive forces for the crystal to have such a high melting point.  And yet when mixed with water, the salt dissolves and as we have learned, breaks up into sodium and chloride ions.  Why does it do this when the crystal has such strong ionic attractions?  The energetics must be more favorable for the ions in water than in the crystalline state.  This is due to the hydration of the ions by water molecules.  The positively charged sodium ions find themselves surrounded by the partially negatively charged oxygens of several water molecules.  The chlorides end up surrounded by the partially positively charged hydrogens of the water molecules. These hydrated ions are sometimes called aquo complexes.  Whenever an ion combines with molecules or other ions to form new ions, the result is called a complex.

Today's experiment involves the qualitative observation of complex formation and utilization of reactions in qualitative analysis schemes. In the classical qualitative scheme to analyze for silver and mercury(I) ions, chloride ion is added to precipitate AgCl and $Hg_2Cl_2$ (mercurous ion is unusual in that it exists in solution as dimers, $Hg_2^{2+}$ rather than as $Hg^+$). Addition of ammonia causes the silver chloride to dissolve as silver ion complexes strongly with ammonia:
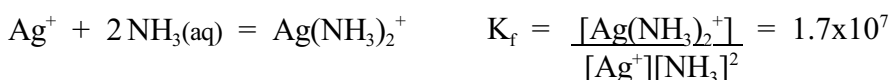
$$AgCl(s) + 2NH_3(aq) = Ag(NH_3)_2^+ + Cl^-$$
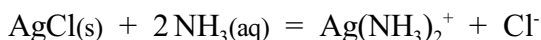
$Hg_2Cl_2$ disproportionates in the presence of ammonia and is easily detected by the black color of mercury produced.

$$Hg_2Cl_2(s) + 2NH_3(aq) = HgNH_2Cl(s) + Hg(l) + NH_4Cl(aq)$$

The decantate containing the silver ammonia complex is acidified to reform the white precipitate of silver chloride.

$$Ag(NH_3)_2^+ + 2H^+ + Cl^- = AgCl(s) + 2NH_4^+$$
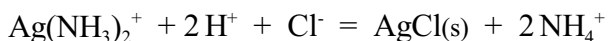
Many formation constants for complexes ($K_f$) have been determined. These may be used to calculate the amounts of complex that will be formed as a function of the concentrations of cations and complexing agents. By utilizing these constants, it is possible to determine if a precipitate will form in the presence of a complexing agent or an acid. Using the silver-ammonia system as an example, it is possible to calculate the concentration of ammonia needed to produce soluble 0.1 M $Ag(NH_3)_2Cl$ from insoluble AgCl.

$$AgCl(s) = Ag^+ + Cl^- \qquad\qquad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$Ag^+ + 2NH_3(aq) = Ag(NH_3)_2^+ \qquad\qquad K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

Combining the two expressions results in the cancellation of silver ion from the equation.
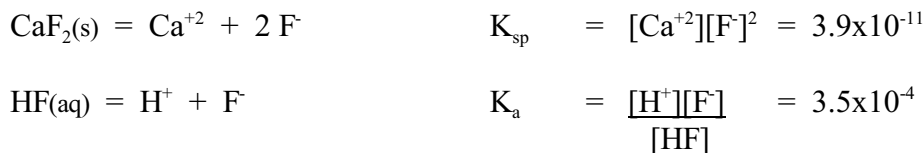
$$K_f K_{sp} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

Solving for $[NH_3]^2$ and assuming that virtually all the silver ion is complexed results in:

$$[NH_3]^2 = \frac{[Ag(NH_3)_2^+][Cl^-]}{K_f K_{sp}} = \frac{(0.10)(0.10)}{(1.7 \times 10^7)(1.8 \times 10^{-10})} = 3.3 \qquad [NH_3] = 1.8\ M$$

For the above example, the ammonia concentration comes out 1.8 M. Because 0.2 M $NH_3$ is used up complexing with the AgCl, the solution should be made a total of 2.0 M in ammonia.

When the anion of a precipitate is the conjugate base of a weak acid (e.g., sulfide from hydrogen sulfide), the precipitate can sometimes be dissolved by the addition of a strong acid. $H^+$

decreases the concentration of the anion by shifting the equilibrium, $HA = H^+ + A^-$, to the left. As the anion concentration decreases, the cation concentration increases. Recall that [anion][cation] = constant. The additional cations are provided by the precipitate as it dissolves. The following example presents the calculations for the concentration of acid necessary to prevent precipitation of 0.1 M $CaF_2$.

$$CaF_2(s) = Ca^{+2} + 2\,F^- \qquad\qquad K_{sp} = [Ca^{+2}][F^-]^2 = 3.9\times10^{-11}$$

$$HF(aq) = H^+ + F^- \qquad\qquad K_a = \frac{[H^+][F^-]}{[HF]} = 3.5\times10^{-4}$$

It is now possible to solve for the concentration, $[H^+]$, necessary to prevent precipitation by combining the two equilibrium expressions in the appropriate way to eliminate fluoride concentration.

$$[H^+] = \frac{K_a[HF]}{[F^-]} = \frac{K_a[HF][Ca^{2+}]^{1/2}}{(K_{sp})^{1/2}} = \frac{(3.5\times10^{-4})(0.20)(0.32)}{6.2\times10^{-6}} = 3.6\ M$$

Thus 0.10 M $CaF_2$ should be soluble in dilute (6 M) HCl.

## Procedure

**A. Qualitative observations.** A series of experiments will be performed to study the possible formation of precipitates and complexes. Experimental observations will be compared to the results of calculations using literature values of equilibrium constants.

1. Transfer about 2 mL (about 40 drops) of 0.1 M $MgCl_2$ solution to 5 test tubes.

2. Add 3 M NaOH dropwise to the first test tube being sure to stir and to make visual observations for each drop. Record any significant changes. Continue until about 20 drops of NaOH have been added.

3. Repeat #2 in the second tube but substitute 3 M $NH_3$ for the NaOH.

4. Repeat #2 in the third tube but substitute 1 M KSCN for the NaOH.

5. Add about 2 mL of 0.1 M $K_4Fe(CN)_6$ to the fourth tube.

6. Add 3 mL of 0.1 M $Na_3PO_4$ to the fifth tube. Record all observations. Continuing with the fifth tube, add 10 drops of 6 M HCl. Be sure to stir and record any significant changes as you proceed.

7. Repeat 1-6 with 0.1 M $CuSO_4$, 0.1 M $Fe(NO_3)_3$ and 0.1 M $Zn(NO_3)_2$.

The tables below contain the pertinent literature data for you to determine if your observations are consistent with the published values for the equilibrium constants. In the ***Results and Discussion*** section, you will be asked to perform a few of the possible calculations to check for

consistency with your observations.

| Solubility Product | | Formation Constants | | Acid Diss. Constants | |
| --- | --- | --- | --- | --- | --- |
| Substance | $K_{sp}$ | Complex | $K_f$ | Substance or ion | $K_a$ |
| $Cu_3(PO_4)_2$ | $1.3 \times 10^{-37}$ | $Cu(NH_3)_4^{2+}$ | $4.8 \times 10^{12}$ | $H_3PO_4$ | $7.5 \times 10^{-3}$ |
| $Mg_3(PO_4)_2$ | $6.3 \times 10^{-26}$ | $Zn(NH_3)_4^{2+}$ | $2.9 \times 10^9$ | $H_2PO_4^-$ | $6.2 \times 10^{-8}$ |
| $Zn_3(PO_4)_2$ | $9.1 \times 10^{-33}$ | $Cu(OH)_4^{2-}$ | $1.3 \times 10^{16}$ | $HPO_4^{-2}$ | $1 \times 10^{-12}$ |
| $Cu(OH)_2$ | $1.3 \times 10^{-20}$ | $Zn(OH)_4^{2-}$ | $2 \times 10^{20}$ | | |
| $Fe(OH)_3$ | $3 \times 10^{-39}$ | $FeSCN^{2+}$ | $1.2 \times 10^2$ | | |
| $Mg(OH)_2$ | $7.1 \times 10^{-12}$ | | | | |
| $Zn(OH)_2$ | $1.2 \times 10^{-17}$ | | | | |

   **B.  Unlabeled Bottles**.  In many "unlabled" test tube experiments where the goal is to identify the contents of the tubes by mixing tubes together, it is common for the reactions involved to be limited to double replacements.  This experiment also involves identification of unlabeled test tubes but the mixtures could result in complex formation as well as double replacement reactions. Based on the information in Part A, you should be able to develop a prediction matrix.  By mixing the possible pairs, you will be able to fill in an observation matrix.  Comparison of the two should enable you to assign identities to the solutions.  Be careful with your comparisons as **observations will depend on the order of mixing**.  Addition of zinc nitrate to sodium hydroxide may yield different observations than when sodium hydroxide is added to zinc nitrate.   Because the observations may depend on the order of mixing, the matrix provided on page 14 has been designed to allow you to enter predictions and observations for both mixing directions.  The seven solutions that will be provided are:

0.1 M $CuSO_4$                      3 M $NH_3$
0.1 M $Fe(NO_3)_3$                 3 M NaOH
0.1 M $MgCl_2$                       1 M KSCN
0.1 M $Zn(NO_3)_2$

   **C. A Qualitative Analysis Scheme.**  For this part of the experiment, you will be given an unknown that could contain one or a mixture of any of the following cations:  $Cu^{2+}$, $Fe^{3+}$, $Na^+$, $Zn^{2+}$. Devise a scheme for the analysis of the mixture.  The results of Part A of this experiment should help you devise this scheme.  Fill in the flow diagram in the *Results and Discussion* section.  Two of the possible ions are colored and at least one of the two can probably be identified or ruled out simply by observing the original mixture.  However, you should develop a scheme that enables you to verify your preliminary conclusions from color and then perform the entire scheme both on a known mixture of all four ions and your unknown.

Name_____Date_____Lab Section_____

## Prelaboratory Problems - *Experiment 1* - Complexes

1.  a.  Should the equivalent of 0.01 M AgBr [$K_{sp}$ = 5x10$^{-13}$] dissolve in 6 M NH$_3$ [$K_f$ for Ag(NH$_3$)$_2^+$ = 1.7x10$^7$]?

    b.  What is the minimum concentration of ammonia that should dissolve AgBr to produce a 0.01 M Ag(NH$_3$)$_2^+$ solution?

2.  What hydrogen ion concentration should be required to dissolve 0.10 M MgF$_2$ if the $K_{sp}$ for magnesium fluoride is 6.8x10$^{-9}$ and $K_a$ for HF is 6.5x10$^{-4}$?

3. For *Part B*, write reactions for as many of the reactions as possible for the Unlabeled Bottles and fill out the *Prediction Matrix*.

Name_____Date_____Lab Section_____

# Results and Discussion - Experiment 1 - Complexes

**A.** **Qualitative observations.** Record any significant observations made during the addition of the reagent to the solution containing the cation. Write net ionic equations that account for your observations.

| Reagent | $Mg^{2+}$ | $Cu^{2+}$ |
|---|---|---|
| NaOH | | |
| $NH_3$ | | |
| KSCN | | |
| $K_4Fe(CN)_6$ | | |
| $Na_3PO_4$ | | |
| $Na_3PO_4$ + 6 M HCl | | |

| Reagent | $Fe^{3+}$ | $Zn^{2+}$ |
|---|---|---|
| NaOH | | |
| $NH_3$ | | |
| KSCN | | |
| $K_4Fe(CN)_6$ | | |
| $Na_3PO_4$ | | |
| $Na_3PO_4$ + 6 M HCl | | |

1.   a.   Use values of $K_{sp}$ and $K_f$ for copper(II) hydroxide and its complex to predict if a precipitate should form in a 0.1 M $Cu^{2+}$ solution that is 3 M in $OH^-$.

     b.   Are the results of 1a consistent with your observations?  Explain your answer.

2.   Repeat 1a and 1b for 0.1 M $Zn^{2+}$ in 3 M $OH^-$.

     a.

     b.

3.  a.  Should $Cu(OH)_2$ precipitate in 3 M $NH_3$ if the original $[Cu^{2+}]$ is 0.1 M (the $K_b$ for ammonia is $1.6x10^{-5}$)?

    b.  Are the results of 3a consistent with your observations?  Explain your answer.

4.  What is the approximate percent of complexed iron in a 0.1 M $Fe^{3+}$ solution containing 1 M KSCN?

5.  Qualitatively account for your observations when 3 M HCl is added to the phosphates of magnesium, copper(II), iron(III) and zinc.  Discuss this in terms of Le Chatelier's principle and the prevailing equilibria.

6.  Refer to your observations on the $Cu^{2+} + SCN^-$ system.  See if you can find any information in the literature on $Cu(SCN)_2$.  Are your observations consistent with the literature information?

**B. Unlabeled bottles.** Seven unlabeled bottles containing the solutions below in some scrambled sequence will be provided.

| | |
|---|---|
| 0.1 M $CuSO_4$ | 3 M $NH_3$ |
| 0.1 M $Fe(NO_3)_3$ | 3 M $NaOH$ |
| 0.1 M $MgCl_2$ | 1 M $KSCN$ |
| 0.1 M $Zn(NO_3)_2$ | |
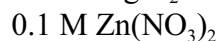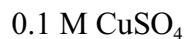
For the 21 possible mixtures of the seven solutions write net ionic equations (NIE). When no reaction is expected, write *NAR* for no apparent reaction. In some cases, a precipitate will form first and then dissolve as a complex is formed. In these cases, write net ionic equations for precipitation and dissolving reactions. Based on these equations, fill in the prediction matrix. Based on your experimental observations, fill in the observation matrix. Compare the two and assign identities to *A - G*. Some of the lines below may be extras.

1.  copper(II) sulfate + iron(III) nitrate

    NIE_____

2.  copper(II) sulfate + magnesium chloride

    NIE_____

3.  copper(II) sulfate + zinc nitrate

    NIE_____

4.  copper(II) sulfate + ammonia

    NIE_____

    NIE_____

5.  copper(II) sulfate + sodium hydroxide

    NIE_____

    NIE_____

6.  copper(II) sulfate + potassium thiocyanate

    NIE_____

7.  iron(III) nitrate + magnesium chloride

    NIE_____

8. iron(III) nitrate + zinc nitrate

   NIE _____

9. iron(III) nitrate + ammonia

   NIE _____

   NIE _____

10. iron(III) nitrate + sodium hydroxide

    NIE _____

    NIE _____

11. iron(III) nitrate + potassium thiocyanate

    NIE _____

    NIE _____

12. magnesium chloride + zinc nitrate

    NIE _____

13. magnesium chloride + ammonia

    NIE _____

    NIE _____

14. magnesium chloride + sodium hydroxide

    NIE _____

    NIE _____

15. magnesium chloride + potassium thiocyanate

    NIE _____

16. zinc nitrate + ammonia

NIE_____

NIE_____

17. zinc nitrate + sodium hydroxide

NIE_____

NIE_____

18. zinc nitrate + potassium thiocyanate

NIE_____

19. ammonia + sodium hydroxide

NIE_____

20. ammonia + potassium thiocyanate

NIE_____

21. sodium hydroxide + potassium thiocyanate

NIE_____

14

Prediction matrix (order of mixing - substance on top added to substance on right)

| $CuSO_4$ | $Fe(NO_3)_3$ | $MgCl_2$ | $Zn(NO_3)_2$ | $NH_3$ | $NaOH$ | $KSCN$ | |
|---|---|---|---|---|---|---|---|
| ☺ | 1 | 2 | 3 | 4 | 5 | 6 | $CuSO_4$ |
| 1 | ☺ | 7 | 8 | 9 | 10 | 11 | $Fe(NO_3)_3$ |
| 2 | 7 | ☺ | 12 | 13 | 14 | 15 | $MgCl_2$ |
| 3 | 8 | 12 | ☺ | 16 | 17 | 18 | $Zn(NO_3)_2$ |
| 4 | 9 | 13 | 16 | ☺ | 19 | 20 | $NH_3$ |
| 5 | 10 | 14 | 17 | 19 | ☺ | 21 | $NaOH$ |
| 6 | 11 | 15 | 18 | 20 | 21 | ☺ | $KSCN$ |

Experimental observation matrix

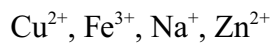| *A* | *B* | *C* | *D* | *E* | *F* | *G* | |
|---|---|---|---|---|---|---|---|
| ☺ | | | | | | | *A* |
| | ☺ | | | | | | *B* |
| | | ☺ | | | | | *C* |
| | | | ☺ | | | | *D* |
| | | | | ☺ | | | *E* |
| | | | | | ☺ | | *F* |
| | | | | | | ☺ | *G* |

Label color_____

$A =$ _____     $C =$ _____     $E =$ _____     $G =$ _____

$B =$ _____     $D =$ _____     $F =$ _____

**C. A Qualitative Analysis Scheme.** 1. Prepare a flow diagram for the analysis of the cations, $Cu^{2+}$, $Fe^{3+}$, $Na^+$, and $Zn^{2+}$.

$$\boxed{Cu^{2+}, Fe^{3+}, Na^+, Zn^{2+}}$$

2. List the steps of your procedure for determining your known (a mixture of all four cations) followed by your observations and molecular and net ionic equations that account for your observations.

Procedure

<u>Observations</u>                                                    <u>Equations</u>

3.  Give your observations and conclusions for your unknown.

4.  Cations present in your unknown (# = _____ ), _____

5.  Some of the *Learning Objectives* of this experiment are listed on the first page of this
    experiment.  Did you achieve the *Learning Objectives*?  Explain your answer.