

EXPERIMENT 6

Competitive Precipitation and Complexation Reactions

This experiment is assigned on page 242 of the textbook.

FOR THE INSTRUCTOR

This experiment can be performed in three ways: (1) as a demonstration/discussion; (2) in the laboratory; and (3) as an alternate version for students who have done and can recall a Qualitative Analysis (qual scheme) set of experiments.

(1) As a demonstration/discussion, many solutions are involved, so as in Experiment 5 I set up racks of test tubes already containing the metal ions called for in the experiments. I normally omit the urea/thiourea set of experiments, since these are a bit more difficult to interpret.

SOLUTIONS REQUIRED (salts required to make 100 L of each solution): Note that starred (*) solutions were also used in a preceding Experiment. Daggered (†) solutions deteriorate; so should be made fresh each year.

1 M AgNO ₃ *	2 M KF (11.6 g)
0.33 M BiCl ₃ (10.5 g; add HCl)	2 M KI† (33.2 g)
0.5 M CuSO ₄ *	0.5 M NaOH (2.0 g)
<0.5 M HgCl ₂ (saturated, 13.6 g)	0.5 M Na ₂ S† (12.0 g 9-hydrate)
1 M LiCl (4.24 g)	0.25 M Na ₄ SiO ₄ *
0.5 M MgCl ₂ *	saturated CO(NH ₂) ₂ †
0.33 M PrCl ₃ (11.8 g 6-hydrate)	saturated CS(NH ₂) ₂ †

FOR THE STUDENTS

In nature (in our physical environment or in cells), we find mixtures of several metal ions with countless numbers of ligands. Although a given metal ion might tend to combine (give a complex or a precipitate) with a given ligand, this may not happen in nature because some other ligand may form a more stable complex or a more insoluble precipitate. In this experiment, we look for some generalizations to help us anticipate, in a complicated mixture, which metal ions will combine with which ligands.

Part I. Competition of Iodide and Fluoride

- A. Prepare a mixture of 10 mL of 2.0 M KI solution with 10 mL of 2.0 M KF solution (AVOID CONTACT WITH ACID! HF IS A VERY DANGEROUS POISON!). Stir well, then put 1 mL of this mixture in each of six test tubes. To each of the six test tubes, add 1 mL of a different one of the following six solutions: 1 M LiCl, 1 M AgNO₃, 0.5 M SrCl₂, 0.5 M HgCl₂, 0.5 M MgCl₂, 0.5 M CuSO₄. Record your results, noting the colors of the products.
- B. Design and carry out some experiments that will enable you to determine what the precipitate is in each case. Identify each precipitate in Step IA.
- C. Which metal ions have fluorides that are less soluble than their iodides? Which metals ions have iodides that are less soluble than their fluorides? Which of the fundamental atomic properties we have used as predictors (Pauling electronegativity, ionic charge, ionic radius, etc.) seems to be most useful to predict the relative solubility of iodides versus fluorides? Use that property to predict the identities of four more insoluble fluorides; four more insoluble iodides. Verify your predictions with your instructor before proceeding.

Part II. Competition of Sulfide and Hydroxide

- A. Take 10 mL of an 0.5 M Na₂S solution. Test its pH. What other anions (besides S²⁻) are present? Put 1 mL in each of eight test tubes. To each of the eight test tubes add 1 mL of a different one of these eight solutions: 1 M LiCl, 1 M AgNO₃, 0.5 M MgCl₂, 0.5 M CuSO₄, 0.5 M SrCl₂, 0.5 M HgCl₂, 0.33 M PrCl₃ (or another *f*-block +3 ion), and 0.33 M BiCl₃. Record the results.
- B. Design and carry out experiments that will enable you to determine the identity of the precipitate in each case.
- C. Which metals form sulfides that are less soluble than their hydroxides or oxides? Which metals prefer to remain as hydrated ions, or to form hydroxides or oxides, rather than to precipitate sulfides? Which fundamental atomic property seems to work best to predict the relative tendency to form sulfides versus hydroxides, oxides, or hydrated ions? Predict four more metals that will have sulfides more insoluble than hydroxides; four more that will have hydroxides more insoluble than sulfides. Verify with your instructor.

Part III. Competition of Urea and Thiourea

- A. Mix 10 mL of a saturated urea $[(\text{NH}_2)_2\text{C=O}]$ solution with 10 mL of a saturated thiourea $[(\text{NH}_2)_2\text{C=S}]$ solution. Stir well, then put 2 mL in each of eight test tubes. To each of these test tubes add a different one of the same eight metal-ion solutions used in Step IIA. Record your results.
- B. Identify your products and write plausible formulas for them.
- C. Which metals react with thiourea in preference to urea? Which prefer to react with urea or stay in hydrated form?
- D. Do you see any relationship between the results of the experiment with the F^-/I^- mixture, that with the $\text{S}^{2-}/\text{OH}^-$ mixture, and that with the urea/thiourea mixture? If so, describe the relationship.

Part IV. Competition of Sulfate and Sulfide

- A. Prepare a mixture of 10 mL of 0.25 M Na_4SiO_4 and 5 mL of 0.5 M Na_2S . (The mixture is now 0.167 M in each.) Put 1.5 mL of this mixture in each of eight test tubes. To each of the eight test tubes add 0.5 mL of one of the eight metal-ion solutions you have been using. Record the results and identify the products.
- B. The largest number of minerals are silicates or sulfides, which presumably arise as the result of competitive precipitation experiments. Draw a periodic table in which you indicate the metals you would expect to find in nature as silicates. (Geochemists refer to these as the lithophile elements.) Indicate the metals that you would expect to find in nature as sulfides. (Geochemists refer to these as the chalcophile elements.) Also indicate any area of the table in which you are not yet able to make predictions.

Alternate Version of this Experiment

This series of questions is for students who have done the qualitative analysis scheme (qual scheme) in general chemistry.

1. List all of the metals (in the general known sample) that precipitate as chlorides in group I (note that these would precipitate as sulfides in group II if you neglected to add the chloride ion). List all of the metals that precipitate as sulfides in group II or as sulfides in group III. List all of the metals that precipitate as hydroxides or oxides in group III. List all of the metals that precipitate as carbonates in group IV. List all of the metals that remain as hydrated ions in group V.
2. Identify the donor atom of the carbonate ion (group IV) and the water molecule (group V). Consolidate your lists from the previous Question 1 into two larger lists: one of metal ions that prefer to precipitate with the sulfide ion (sulfur donor atom); the other of metal ions that prefer to coordinate with oxygen donor atoms.
3. Which of the fundamental atomic properties we have used as predictors (Pauling electronegativity, ionic charge, ionic radius, etc.) would be most useful to separate the metal ions that tend to coordinate with sulfur donors from the metal ions that tend to coordinate with oxygen donors?
4. Use your relationship to predict six more metal ions that should belong to each of the two lists from Question 2. Can you also decide which of the six additional

oxygen-preferring metal ions would fall in qual scheme group III, which in qual scheme group IV, and which in qual scheme group V? (This solution requires principles explained earlier in the text.)

5. The largest number of minerals are silicates or sulfides, which presumably arise as the result of competitive precipitation experiments. Draw a periodic table in which you indicate the metals you would expect to find in nature as silicates. (Geochemists refer to these as the lithophile elements.) Indicate the metals that you would expect to find in nature as sulfides. (Geochemists refer to these as the chalcophile elements.) Also indicate any area of the table for which you are not yet able to make predictions.