Experiment 6: Competitive Precipitation Reactions[1]

1.a. Prepare a mixture of 3 mL of 2.0 M KI solution with 3 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 $AgNO_3$, 0.5 M $SrCl_2$, saturated $HgCl_2$, 0.5 M $MgCl_2$, 0.5 M $CuSO_4$. Record your results, noting the colors of the products.

1.b. Design and carry out some experiments that will enable you to determine what the precipitate is in each case. Identify each precipitate in part 1.a.

1.c. Which metal ions have fluorides that are less soluble than their iodides? Which metal ions have iodides that are less soluble than their fluorides? Which of the fundamental atomic properties that we have used as predictors (Pauling electronegativity, ionic charge, ionic radius, etc.) seems to be most useful in predicting the relative solubility of iodides versus fluorides? Use it to predict the identities of two more insoluble fluorides; two more insoluble iodides. Verify your predictions with your instructor before proceeding.

2.a. In the hood, test the pH of a 0.5 M Na_2S solution. What other anions (besides S^{2-}) are present? Put 1 mL in each of eight test tubes. To each of the eight add 1 mL of a different one of these eight solutions: 1 M LiCl, 1 M $AgNO_3$, 0.5 M $SrCl_2$, saturated $HgCl_2$, 0.5 M $MgCl_2$, 0.5 M $CuSO_4$, 0.33 M $LaCl_3$ (or another *f*-block +3 ion), and 0.33 M $BiCl_3$. Record the results.

2.b. Carry out experiments that will enable you to determine the identity of the precipitate in each case.

2.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 in predicting the relative tendency to form sulfides versus hydroxides, oxides, or hydrated ions? Predict two more metals that will have sulfides more insoluble than hydroxides; two more that will have hydroxides more insoluble than sulfides. Verify with your instructor.

3.a. Mix 8 mL of a saturated urea [$(NH_2)_2C{=}O$] solution with 8 mL of a saturated thiourea [$(NH_2)_2C{=}S$] 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 part 2.a. Record your results.

3.b. identify your products and write plausible formulas for them.

3.c. Which metals react with thiourea in preference to urea? Which prefer to react with urea or to stay in hydrated form?

4. Do you see any relationship among the results of the experiment with the F^-/I^- mixture and that with the S^{2-}/OH^- mixture and that with the urea/thiourea mixture? If so, give the relationship.

5.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

[1] Adapted from *Inorganic Chemistry*, G. Wulfsberg, University Science Books, Sausolito, CA, 2000.

tubes add 0.5 mL of one of the eight metal-ion solutions you have been using. Record the results and identify the products.

5.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 tables for which you are not yet able to make predictions.