Experiment 2: Some Reactions Of Cations[1]

The chemistry of cations can be generalized to some extent. Today, we are interested in the chemistry of the elements under a very common set of circumstances: when the elements have positive oxidation numbers and are in aqueous solution. We will start with the presumption that an element in a positive oxidation state is present as a cation. (Of course, we cannot obtain cations by themselves, so in this experiment we will use the chlorides of these elements -- the chloride anion does not substantially affect the results of most of these experiments.) We will observe a most elementary reaction of these chlorides -- dissolving them in water -- and will find that something does indeed happen chemically when this experiment is performed. Finally, we will try to find periodic trends in the degree to which this chemical reaction occurs, by relating reactivity to cation charge, radius and electronegativity.

1.a. Take five test tubes; to each add 2 to 3 mL of distilled water. To the first test tube add *nothing*. Measure the pH of the distilled water using first long-range and then short-range pH papers. In your notebook, record the pH in a data table similar to the one below. (Do not presume that the pH of the distilled water is 7.0!) Also, feel the test tube to note qualitatively the temperature of the distilled water.

1.b. To the second test tube add LiCl (approximately the size of a pea). Stir until it is dissolved, then measure and record its pH as before. Also, note whether there is any detectable change in temperature.

1.c. To the third test tube add a similar amount of dry $ZnCl_2$, stir to dissolve, measure its pH, and record any temperature change. To the fourth test tube add a similar amount of *fresh, anhydrous* $AlCl_3$, stir to dissolve, measure the pH, and record any temperature change.

1.d. In the glovebox, you will find containers of $TiCl_4$ and PCl_3. You should obtain a sample (~0.5 mL) of each making sure that they are well sealed before bringing them out of the box. In the hood, **Cautiously** using a test tube holder, add the $TiCl_4$ into a large test tube of DI water. Measure the pH of the solution and (using a moistened pH paper) of the gas being evolved from the test tube; cautiously feel the bottom of the test tube to note any temperature change. Record your pH's and observations of temperature changes and any other visible or audible changes in a table similar to that below.

Solute	Cation radius	Electronegativity	Charge	pH	Observations
Distilled H_2O					
LiCl					
$ZnCl_2$					
$AlCl_3$					
$TiCl_4$					

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

2. What do you think happened in the test tubes in which reactions occurred? In your notebook, write plausible chemical equations that would account for your observations. What might be the precipitate that you saw?

3. Fill in the cation radius, electronegativity, and the oxidation numbers (cation charges) of the (nonchlorine) elements in the table, then look at the three periodic properties listed there (radius of the cation, Pauling electronegativity of the cation, and cation charge). Which one of these varies most significantly in this series of four compounds? Finally, decide how the tendency of a cation to undergo the reaction you described in part 2 depends on this periodic property.

4. "Sky-writing" involves spraying $TiCl_4$ from an airplane into the air. Explain the chemistry of sky-writing. How would you have to handle compounds like $TiCl_4$ to prevent this reaction from happening while filling the plane with the metal halide?

5. In the hood, carry out the same sort of experiment, adding spatula-tipfuls (or a few drops taken using a disposable pipet) of the following compounds to 2 –3 mL of DI water. What is the significant periodic variable in this series of compounds? Can you write a conclusion relating the reaction tendency in this series of compounds to this variable?

Solute	Cation radius	Electronegativity	Charge	pH	Observations
$BiCl_3$					
$SbCl_3$					
PCl_3					

6. Design and carry out an experiment to determine whether the Pauling electronegativity of the cation has any effect on this reaction tendency. Use appropriate chlorides from the following list, <u>but do not use them all</u>: $CaCl_2$, $SrCl_2$, $MnCl_2$, $FeCl_2$, $ZnCl_2$, $SnCl_2$, $Pb(NO_3)_2$ and $Hg(NO_3)_2$ (chlorides not suitable here), $LaCl_3$ (or other *f*-block trichoride), and $BiCl_3$. *Hint*: Rather than starting by testing all these chlorides look at the periodic properties (cation charge, radius and electronegativity) of the cations first, and pick out only the set or sets of compounds to test that will give you the comparison that you want. Keep in mind that electronegativity values can vary by as much as 0.3 units. Think Carefully **– Do Not Use All of the Compounds!**

7. Double-check your conclusion in part 4 by checking the results with these two Group 14/IVA chlorides: $SnCl_4$ and CCl_4. First use your principles to predict what will happen, then do the test. Can you explain any discrepancy between theory and observation?

8. A far-too-frequent experience of people who make up solutions of metal salts such as $SnCl_2$, $Hg(NO_3)_2$, and $BiCl_3$ and get a cloudy solution is to assume that their compound or water was contaminated; hence they throw out the solution and try again, only to get the same result. Looking at the equations you wrote in part 2, suggest what must be done to get clear solutions of these metal ions. Test your answer by trying it with one of the above three salts.