EXPERIMENT 2

Some Reactions of Cations

This experiment is assigned on page 44 of the textbook.

FOR THE INSTRUCTOR

This experiment can be performed in three ways.

1. The instructor shows the video titled "Some Reactions of Cations," found at uscibooks.aip.org/videos/, and the students, in groups, record the re-sults and discuss their conclusions, filling out the worksheets.
2. The instructor demonstrates the reactions and the students, in groups, record the results and their conclusions, and answer the questions. Since it is diffi-cult for students in a classroom to see pieces of pH paper, these results can be written on the board. But we ask students in the front row to verify by CARE-FULLY touching reaction vessels in which significant heat is evolved.
3. The students perform the experiment in the laboratory, and the students, in groups, record the results and discuss their conclusions, filling these out in a lab report.

SOLIDS REQUIRED. These should be anhydrous unless otherwise stated. Those indicated by # should be stored in an airtight manner, for example, in Erlenmeyer flasks with tightly-fitting rubber septa. In a glove bag we prepare individual portions of $AlCl_3$ and $TiCl_4$ in micro test tubes capped with septa.

$AlCl_3$#	$BiCl_3$#	CCl_4
$CaCl_2$, hydrated	$FeCl_2$, hydrated	HCl, conc.
LiCl	$Hg(NO_3)_2$, hydrated	$MnCl_2$, hydrated
PCl_3	$Pb(NO_3)_2$, hydrated	$PrCl_3$, hydrated*
$SbCl_3$#	$SnCl_4$	$SrCl_2$, hydrated
$TiCl_4$#	$ZnCl_2$#	

*or other *f*-block hydrate.

FOR THE STUDENTS

In this experiment (or demonstration and discussion) we investigate the chemistry of 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. Since we cannot obtain cations by themselves, we generally use the chlorides of these elements, since the chloride anion does not substantially affect the results.

We observe a most elementary reaction of these chlorides—dissolving them in water—and find that something may indeed happen chemically to the cations when this is done. Finally, we will try to find periodic trends in the degree to which this chemical reaction occurs, by relating the tendency to react to the basic periodic properties of cations discussed in Chapter 1.

Part I

A. 1. Take five test tubes; to each add 2–3 mL of distilled water. Add nothing to the first test tube. Measure the pH of the distilled water using first long-range and then short-range pH papers. Record the pH in the data table 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.

2. Add LiCl (enough to cover the larger end of a standard nickel spatula) to the second test tube. Stir until it is dissolved; then measure and record its pH as before. Also note whether there is any detectable change in temperature.

3. 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.

4. Go to the hood to obtain a micro test tube (closed with a tight stopper or a septum) containing 0.5 mL of $TiCl_4$. Cautiously open the test tube and pour the contents into the (larger) fifth test tube of distilled water. Stir. Measure the pH of the solution and (using 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 values and observations of temperature changes and any other visible or audible changes in the table below.

Solute	Cation radius	χ_P	Charge	pH	Observations
Distilled water					
LiCl	90	0.98			
$ZnCl_2$	88	1.65			
$AlCl_3$	67	1.61			
$TiCl_4$	74	1.54			

B. 1. What do you think happened in the test tubes in which reactions occurred? On the report sheet, write plausible chemical equations that would account for your observations.

2. Fill in the oxidation numbers (cation charges) of the (non-chlorine) elements in the above table, then look at the three periodic properties listed there (radius of the cation, Pauling electronegativity χ_P 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 Step B.1 depends on this periodic property. Write your conclusion on the report sheet.

3. "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?

Part II

A. In the hood, carry out the same sort of experiment, adding spatula tipfuls (or a few drops taken using a dry eyedropper) of the following compounds to 2–3 mL of distilled water. Record the results (and the cation charges) in the table below.

Solute	Cation radius	χ_P	Charge	pH	Observations
$BiCl_3$	117	2.02			
$SbCl_3$	90	2.05			
PCl_3	(~66)	2.19			

B. What is the significant periodic variable in this series of compounds?

C. Can you write a conclusion relating the reaction tendency in this series of compounds to this variable?

Part III

A. Design and carry out an experiment to determine whether the Pauling electronegativity of the cation has any effect on this reaction tendency. Use some, but not all, of the chlorides from the following list: $CaCl_2$; $SrCl_2$; $MnCl_2$; $FeCl_2$; $ZnCl_2$; and $SnCl_2$ (estimated cation radius of 126 pm); $Pb(NO_3)_2$ and $Hg(NO_3)_2$ (chlorides not suitable here); and $PrCl_3$ (or other *f*-block trichloride) and $BiCl_3$. Hint: Rather than starting by testing all of these chlorides, look at the periodic properties 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.

B. Double-check your conclusion in **Part I.B.2** by checking the results with these two Group 14/IV 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?

C. A far-too-frequent experience of people who have to make up solutions of metal salts such as $SnCl_2$, $Hg(NO_3)_2$, $BiCl_3$, and so on, 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 I.B.1,** 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.

SOME REACTIONS OF CATIONS WORKSHEET

Name of team ______________________

Members of team ______________________

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Your goal: To discover connections between:

- Your observations,
- Certain properties of cations,
- Trend in reactivity of the cations.

Part I

Write your observations in the table.

Solute	Cation radius	Electro-negativity	Charge of cations	pH	Observations
H_2O	—	—	—		
LiCl	90	0.98			
$ZnCl_2$	88	1.65			
$AlCl_3$	67	1.61			
$TiCl_4$	74	1.54			

Answer the following questions.

1. What do you think happened in the test tubes in which reactions occurred? Write a plausible (not necessarily correct) **chemical equation** for the reaction that occurred with the most reactive cation.

2. Which atomic variable (**electronegativity, charge of the cation, or size of the cation**) varies most in this set of cations?

3. Does an **increase** in that atomic variable produce an **increase** in reactivity, a **decrease** in reactivity, or have **no effect** on the reactivity of cations?

SOME REACTIONS OF CATIONS WORKSHEET

Name of team ________________________

Part II

Write your observations in the table.

Solute	Cation radius	Electro-negativity	Charge of cations	pH	Observations
$BiCl_3$	117	2.02	—		
$SbCl_3$	90	2.05			
PCl_3	(~66)	2.19			

Answer the following questions.

1. What atomic variable is responsible for the changes in reactivity observed? (Note: You do not need to write a new chemical equation. This reaction is the same type of reaction you observed in Part I.

2. Does an **increase** in that atomic variable produce an **increase** in reactivity, a **decrease** in reactivity, or have **no effect** on the reactivity of cations? Does an increase in that atomic variable produce an increase in reactivity, a decrease in reactivity, or have no effect on the reactivity of cations?

SOME REACTIONS OF CATIONS WORKSHEET

Name of team ________________________

Part III

Design an experiment to determine what role, if any, the electronegativity of the cation plays.

Your group must select a small set of two or three salts that you want to test, and write a sentence justifying why you chose that st. The possible sets of salts to test, the electronegativity of their cation elements, and the radii of their catons are listed below.

Salts	Cation electronegativity	Charge radius
$CaCl_2$	1.00	114
$SrCl_2$	0.95	132
$PrCl_3$	1.13	113
$MnCl_2$	1.55	97
$FeCl_2$	1.83	92
$ZnCl_2$	1.65	88
$Hg(NO_3)_2$*	2.00	116
$SnCl_2$	1.80	(about 110)
$Pb(NO_3)_2$*	1.87	133
$BiCl_3$	2.02	117

*Substituted for the chloride, since the chloride is unsuitable (insoluble).

Answer the following questions:

1. The two or three salts that our group wants to test are:

2. The reason we chose this set is: