EXPERIMENT 4

Some Reactions of Oxo Anions

This experiment is assigned on page 129 of the textbook.

FOR THE INSTRUCTOR

This experiment is best performed as a demonstration-discussion. The instructor measures the pH's of the solutions and the students, in groups, record the results, discuss their conclusions, and record them in their reports. As an alternative with no solutions required, the instructor could present the pH's of the solutions and asks the students, in groups, to discuss these results and report their conclusions.. (NOTE: no worksheets have been provided).

SOUTIONS REQUIRED: Quantities required to make 10 mL of aqueous solutions are listed. Solutions followed by daggers (†) slowly oxidize, so should be remade in the following year.

0.33 M Na_3AsO_3† (0.43 g $NaAsO_2$ + 0.27 g NaOH)

0.33 M Na_3AsO_4 (1.04 g $Na_2HAsO_4 \cdot 7H_2O$ + 0.13 g NaOH)

0.5 M Na_2CO_3 (0.53 g)

4–6% NaClO solution (bleach)†

1 M $NaClO_4$ (1.40 g 1-hydrate)

0.5 M K_2CrO_4 (optional)

<1 M $NaIO_3$ (saturated, 1.98 g)

<1 M $KMnO_4$ (saturated, optional)

1 M $NaNO_2$† (0.69 g)

1 M $NaNO_3$ (0.85 g)

0.33 M K_3PO_4 (0.95 g 8-hydrate)

0.5 M Na_2SO_3† (0.63 g)

0.5 M Na_2SO_4 (1.61 g 10-hydrate)

0.25 M Na_4SiO_4 (0.46 g)

0.33 M K_3VO_4 (optional)

TYPICAL RESULTS

CO^- pH 10 versus ClO_4^- pH 5.

NO_2^- pH 6.5 versus NO_3^- pH 5

SO_3^{2-} pH 8.5 versus SO_4^{2-} pH 5.5.

AsO_3^{3-} pH 13 versus AsO_4^{3-} pH 12.

SiO_4^{4-} pH 12.5; IO_3^- pH 5.5

FOR THE STUDENTS

The principles we have developed in Chapter 2 to predict the acidity of cations are most useful when the elements are not in high oxidation states. Our best approach to systematizing the chemistry of elements in high oxidation states in aqueous solution is to start with them in their "final" form—as oxo anions. In this experiment, we will try to find simple but useful principles for predicting the basicity of oxo anions.

Part I

A. Using long- and short-range pH test papers, the instructor checks the pH of the distilled water, then measures and compares the pH values of solutions of the following two pairs of salts of oxo anions: $NaClO$ and $NaClO_4$; Na_2SO_3 and Na_2SO_4.

B. All of these salts contain oxo anions having general formulas MO_x^{y-}. In each pair of compounds, what component of the general formula are we varying? What effect does this variation have on the pH of the solutions?

C. Predict which of each of the following pairs of salts will have the highest pH: $NaNO_2$ or $NaNO_3$; Na_3AsO_3 or Na_3AsO_4. Report your predictions to the instructor, who may test your hypothesis by measuring and comparing the pH values within each pair of salts.

D. What type of reaction is occurring here to produce the pH values observed? The group shoud write an equation to illustrate this type of reaction, using the most reactive of the above oxo anions as an example.

E. Can the group suggest any physical reason for the relationship of this reaction tendency to the structural variable identified in **B**? Suggest your reason to the instructor.

Part II

A. The group should propose experiments to determine the effect of the charge $-y$ of an oxo anion on its basicity. The group may use the data from Part I**.** In addition, solutions of the following salts may also be tested: Na_3PO_4; Na_4SiO_4; and $NaIO_3$.

B. The instructor will provide the additional data you want. What relationship of charge and basicity do you deduce? How would you explain this relationship?

C. The group should predict the trend in pH values of the following series of solutions, two of which are too intensely colored to be tested by pH paper: K_3VO_4, K_2CrO_4, and $KMnO_4$.

D. If a pH meter is available, the instructor could check the pH values of these solutions. If not, the instructor can provide them.

QUESTIONS TO ANSWER ABOUT PARTS I AND II

A. Below are listed the oxo anions of the later *p*-block elements in their highest oxidation states. Note that the number of oxygen atoms (oxo groups) changes down a group.

CO_3^{2-}	NO_3^{-}			
SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^{-}	
GeO_4^{4-}	AsO_4^{3-}	SeO_4^{2-}	BrO_4^{-}	
SnO_6^{8-}	SbO_6^{7-}	TeO_6^{6-}	IO_6^{5-}	XeO_6^{4-}

How could you explain the fact that the number of oxo groups does not remain constant in a group?

B. Note that on going down a group, not only the number of oxo groups but also the charge on the oxo anion changes. Do the effects on basicity of these two changes work in the same direction (i.e., reinforce each other)? Or do the two changes have opposite effects on the basicity of the oxo anions? If the latter is the case, which of the two changes is dominant as you go down a group? If necessary, ask the instructor to test some additional solutions to add to your data (Suggestion: Na_2CO_3).

C. Which oxo anion tabulated in Question A should be the most strongly basic?