

Experiment 3: Some Reactions Of Oxo Anions¹

The principles we have developed to predict the extent of hydrolysis of cations are most useful with the metallic elements when they are in not too high an oxidation state. (Ti^{4+} does not exist in aqueous solution as it has hydrolyzed to TiO_2 .) When we deal with nonmetals or metals in high oxidation states, the notion of a "cation" of the nonmetal or metal is too far divorced from reality to enable us to make reasonably accurate predictions -- for one thing, only limited numbers of "cationic" radii for such species have been tabulated. Our best approach to systematizing the chemistry of nonmetals in aqueous solution with positive oxidation numbers 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 some of their properties.

1. Using long- and short-range pH test papers, check the pH of the distilled water. Then measure and compare the pH's of solutions of the following two salts of oxo anions: NaClO and NaClO_4 . Likewise, measure and compare the pH's of solutions Na_2SO_3 and Na_2SO_4 . All these salts contain oxo anions having the general formula 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? Predict which of each of the following pairs of salts will have the higher pH: NaNO_2 or NaNO_3 ; Na_3AsO_3 or Na_3AsO_4 . Test your hypothesis by measuring and comparing the pH's within each pair of salts.
2. What type of reaction is occurring here to produce the pH's observed? Write an equation to illustrate this type of reaction, using the most reactive of the above oxo anions as an example.
3. Can you suggest any physical reason for the relationship of this reaction tendency to the structural variable you investigated in part 1?
4. Design an experiment to determine the effect of the *charge* - y of an oxo anion on its basicity, and carry out the experiment. You may use the data from part 1; in addition, solutions of the following salts are available: K_3PO_4 , Na_4SiO_4 , NaIO_3 , Na_2CO_3 . (You may decide that you have enough compounds to set up two experiments.) What relationship between charge and basicity do you observe? How would you explain this relationship?

¹ Adapted from *Inorganic Chemistry*, G. Wulfsberg, University Science Books, Sausalito, CA, 2000.

5. Predict the trend in pH's of the following series of solutions, two of which are too intensely colored to be tested by pH paper (A pH meter is available): Na_3VO_4 , K_2CrO_4 , KMnO_4 .
6. 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. How would you explain the fact that the number does not remain constant?



7. Note that down a group, not only the number of oxo groups but also the charge on the oxo anion (MO_x^{y-}) changes. Looking at your previous conclusions, would you expect these simultaneous changes in structure of oxo groups (increasing number of oxygens and increasing negative charge) to have the same effects on basicity (i.e., to reinforce each other's effects)? If so, describe the basicity trend for oxo anions down a group of the periodic table. Or would you expect the two changes to have opposite effects on the basicity of the oxo anions? If the latter is the case, you need to determine which of the two effects is dominant. To do this, compile the pH's of all the oxo anions listed above for which you have data. What is the observed basicity trend for oxo anions down a group of the periodic table?
8. Putting together all your trends, identify the oxo anion listed in part 6 that would most strongly undergo the type of chemical reaction you wrote in part 2.