Periodic Trends: Acids/Bases and Oxidation/Reduction

(Adapted from ***Microscale General Chemistry Laboratory with Selected Macroscale Experiments*, Second Edition** by Zvi Szafran, Ronald M. Pike and Judith C. Foster, Wiley)

Objectives:

1. Experimentally determine whether the oxide of an element is acidic or basic.
2. Determine the periodic trend or pattern for the oxides.
3. Determine which halogens are the strongest oxidants.
4. Determine the periodic trend in oxidation strength.
5. Use negative controls to determine whether a reaction has occurred or not.

Prior Reading in Chemistry 3rd Edition by Julia Burdge

Chapter 7.7 Periodic Trends
Chapter 16.11 Properties of metal hydroxides
Hydrohalic Acid Strength Chapter 16.9

Introduction

The chemical elements are arranged in a systematic manner that we know as the Periodic Table of the Elements. The Periodic Table places elements with the same chemical properties in the same column in ascending order of mass. These columns are known as families or groups. For example, the first column (left-most) of the Periodic Table is known as the alkali metals or Group 1. Physical properties usually vary smoothly down a family. For example, the boiling point of the alkali metals are:

Li: 1317 ºC Na: 892 ºC K: 774 ºC Rb: 701 ºC Cs: 685 ºC

The trend is a decrease in boiling point as we move down the group, that is, as the molar mass of the metals increases. (Why might that be?). A major goal of chemists is to explain these trends and to account for any deviations.

Elements in the same row of the Periodic Table are said to be in the same period. Moving across the period one observes trends in the physical and chemical properties of the elements, although anomalies are more frequently observed. For example, note the following trend in the electronegativities of the third period elements:

Na: 1.0 Mg: 1.3 Al: 1.5 Si: 1.8 P:2.1 S: 2.4 Cl: 2.9

Part A. Periodic Trends in the oxides

In this laboratory we will examine a periodic trend in the oxides of the second and third period elements. These oxides form either acidic or basic solutions in water. An aqueous acidic solution is one that contains more H_3O^+ ions than OH^- ions. An aqueous basic solution is one that contains more OH^- ions than H_3O^+ ions. When an oxide dissolves in water, it may react with the water in such a way that it generates either H_3O^+ or OH^-, making the solution either acidic or basic.

$$Al_2O_3\ (s) + 7\ H_2O\ (l) \rightarrow 2\ Al(OH)_4^-\ (aq) + 2\ H_3O^+ (aq)$$

$$Tl_2O\ (s) + H_2O(l) \rightarrow 2\ Tl^+ (aq) + 2\ OH^-\ (aq)$$

You will test several oxides across the second and third periods for the formation of acidic or basic solutions. The presence of acid or base can be detected with litmus paper or pH paper (universal indicator paper). Based on your results, you will describe the periodic trend.

Part B. Oxidation/Reduction Properties of the Halogens

The elemental form of the halogens is X_2, for example, elemental fluorine is F_2. In this form, the halogens often behave as oxidants, that is, they will take electrons from other substances and form the corresponding halide ion. For example, F_2 is an oxidant that can form fluoride (F^-) ions. The simplest of these reactions is when a halogen of one element reacts with a halide of another element. For example:

$F_2 + 2\ Br^- \rightarrow 2\ F^- + Br_2$

In this reaction, fluorine, F_2, is a stronger oxidant than bromine, Br_2, and so fluorine oxidizes the bromide ions to form fluoride ions and bromine. Your goal is to determine which halogens are the strongest oxidants and whether or not there is a consistent trend.

Procedure

Part A: Acid-Base Properties of the Second and Third Periods

One can determine whether a solution is acidic or basic by testing a drop of the solution on red or blue litmus paper. A drop of solution can be transferred from its container to the litmus paper using a glass stir rod. Acidic solutions turn blue litmus paper red, while basic solutions turn red litmus paper blue. Universal indicator or "pH" paper can also be used. The color of the wetted pH paper is compared to the color key on the side of the container to determine the pH.

Some of your solutions may be only slightly acidic or slightly basic, making the color change difficult to see. In this case, use two pieces of blue litmus paper to test for acid and two pieces of red litmus paper to test for base. Wet one piece of blue litmus paper with water and the other with your solution and compare the two pieces. If there is no difference in their appearance, the test is negative for acid. Now test with red litmus paper, again wetting one piece with water and the other with your solution. If pH paper is used, then only two pieces of pH paper are needed. Compare the pH paper wetted with water to paper wetted with your solution. Then compare both to the color key on the pH paper container.

In the following reactions, you will test aqueous (water) solutions of a number of oxides across the second and third periods to see if they are acidic or basic. Record the results of your tests and any observations that seem interesting or important.

Reaction 1: You will predict whether Na_2O forms an acidic or basic solution with water after you complete reactions 2 – 6.

Reaction 2: Calcium oxide, CaO
Calcium oxide will be used in this step instead of magnesium oxide, as MgO is insoluble in water and beryllium oxide, BeO, is quite toxic.

Fill the tip of a small spatula with calcium oxide powder, CaO, and place the calcium oxide in a 10 x 75 mm test tube. (This will be roughly 10 mg of calcium oxide.) Dropwise, add approximately 1 mL (20 drops) of water. The calcium oxide can be mixed with the water by firmly holding the top of the test tube in one hand while tapping the bottom of the test tube with the pointer finger of the other hand. Test the resulting solution to see if it is acidic or basic.

Reaction 3: Boron Oxide, B_2O_3
Fill the tip of a small spatula with boron oxide and place the oxide in a 10-75 mm test tube. (If boron oxide is not available, $B(OH)_3$, may be used instead.) Add 1 mL of water dropwise (20 drops). Mix. Test the resulting solution.

Reaction 4: Carbon dioxide, CO_2
Set up a beaker with ~20 mL of water. Add 1 or two "pellets" of dry ice, using tweezers or tongs to handle the dry ice. Allow the dry ice to "bubble" the water and cool it for a couple of minutes. While there is still dry ice present and the water is cold, test using litmus or pH paper. Add more pellets of dry ice if needed.

Reaction 5: Phosphorous pentoxide, P_4O_{10}
Your instructor will perform this reaction as a demonstration. For historic reasons, this compound is known as phosphorous pentoxide. However, the actual formula is P_4O_{10} and the compound can also be identified as tetraphosphorousdecoxide.

SAFETY NOTE: Phosphorous pentoxide is extremely corrosive! Do not allow it to contact your skin under any circumstances. Wear plastic gloves.

Place approximately 10 mg of phosphorous pentoxidein a large test tube. Dropwise, add 1 mL of water. Mix the phosphorous pentoxide and water and test.

Reaction 6: Sulfur dioxide, SO_2
Sulfur dioxide is a gas. We will generate SO_2 from sulfur by heating the sulfur in air. The sulfur and the oxygen in the air combine to form SO_2. We will moisten the litmus or pH paper ahead of time and allow the SO_2 gas to form acid or base in the water that moistens the paper.

SAFETY NOTE: Do this reaction in the hood!

Place a spatula tip full of sulfur into the bottom of a 10 x 75 mm test tube. Moisten a piece of blue litmus paper and insert it into the top portion of the test tube so that it sticks to the wall of the tube. You may use a glass stir rod or clean spatula tip to push the litmus paper fully into the tube. Moisten a piece of red litmus paper and insert it opposite the blue litmus paper. If you are using universal indicator paper (pH paper), you will only need one piece of moistened paper.

Clamp the test tube to a ring stand and place a Bunsen burner underneath. Using the Bunsen burner, heat the sulfur until it melts and begins to react with the oxygen in the tube. Give the sulfur dioxide time to move up the tube and react with the water in the moistened litmus or pH paper. **As soon as you observe a color change in the litmus or pH paper, turn off the gas to the Bunsen burner.** Record your observations. Allow the test tube a few minutes to cool before removing it with your test tube tongs.

Reaction 7: Chlorine oxides
Chlorine oxides are extremely dangerous and cannot be safely handled in this lab. The end result of the reaction of Cl_2O_7, dichlorineheptoxide, and water is the formation of $HClO_4$, perchloric acid. Predict whether a solution of this compound with water will be acidic or basic.

Part B
We will look for evidence of oxidation of the halides (fluoride, F^-, chloride, Cl^-, bromide, Br^-, and iodide, I^-) when they are mixed with the halogens (chlorine, Cl_2; bromine, Br_2; and iodine, I_2). (See the data table for Part B.) Elemental fluorine, F_2, is extremely dangerous and difficult to produce, so it will not be used. Fluoride, the halide form is much less dangerous.

The halogens, being neutral and nonpolar dissolve better in a nonpolar solvent such as toluene, whereas the ions, being charged, dissolve better in water. The color of the toluene layer indicates what species is present. In toluene, chlorine is colorless or light yellow, bromine is red-orange, and iodine is purple. Since the two solvents, toluene and water, do not mix readily, the mixture must be triturated (forced to mix by vigorous stirring), or by using an eyedropper or pipet to take up the lower layer (water) and drop it on top of the upper layer; as the drops fall through, the solutes can react.

The vigorous mixing (trituration) may cause the appearance of the aqueous and toluene phases to change, even if there is no oxidation reaction. How can we be sure that what we are seeing is a reaction? The simplest way to solve this problem is to perform what is called a *control experiment*. A control experiment is an experiment where the outcome is known in advance. For example, if we mix a halogen with pure water, then we know that there will be no reaction, since there is no halide with which the halogen can react. Pure water serves as a *negative control*, that is, it shows us what the combination of halogen, water, and toluene look like in the *absence of a reaction*. Since the aqueous potassium halide solutions (KF, KCl, KBr, or KI solutions) look like water, we will assume that if the combination of halogen, aqueous potassium halide solution, and toluene look like the negative control, then there has been no reaction. Note that the negative control experiment must be performed with each halogen solution. (See the data table for Part B.)

ALL REACTIONS SHOULD BE PERFORMED IN THE HOOD.

Reaction 1: Preparation of Chlorine, Cl_2

- Place about 1 mL of chlorine laundry bleach in a 10x75 mm test tube. Chlorine bleach contains about 5% sodium hypochlorite, NaOCl, with the other 95% being made up of inert materials, mostly water. Add 1 mL (or 20 drops) of toluene. A two-layer system should format this point. Note the color of toluene (top) and water (bottom) layers.
- In the hood, acidify the system with 500 µL (or 10 drops) of 6M HCl, and triturate with a spatula. What indication do you have the chlorine has formed, and dissolved in the toluene layer? Record your observations. Do not discard this test tube, it will be used later.

Reaction 2: Reactivity of Chlorine

Record your observations for each sample.

- Place about 1 mL of deionized water in a 10x75 mL test tube. Add one-quarter of the upper toluene layer (with chlorine in it) prepared in Reaction 1 above, using a Pasteur pipet. Agitate the test tube for a moment.
- Place about 1 mL of 0.1 M potassium fluoride, KF, solution in a 10x75 mL test tube. Add one-quarter of the upper toluene layer (with chlorine in it) prepared in Reaction 1 above, using a Pasteur pipet. Agitate the test tube for a moment.
- Perform the same reaction again, but this time using about 1 mL of 0.1 M KBr solution.
- Perform the same reaction again, but this time using about 1 mL of 0.l M KI solution instead of KBr.

Reaction 3: Reactivity of Bromine

Record your observations for each sample.

- Place about 1 mL of deionized water, in a 10x75 mm test tube. Add about one mL of saturated bromine water, using a Pasteur pipet. Add 0.5 mL of toluene, and agitate the test tube for a moment.
- Place about 1 mL of 0.1 M KF solution, in a 10x75 mm test tube. Add about one mL of saturated bromine water, using a Pasteur pipet. Add 0.5 mL of toluene, and agitate the test tube for a moment. Has a reaction taken place?
- Perform the same reaction again, but this time using about 1 mL of 0.1 M KCl solution instead of the KF.

- Perform the same reaction again, but this time using about 1 mL of 0.1 M KI solution.

Reaction 4: Reactivity of Iodine

Record your observations for each sample.

- Place about 1 mL of deionized water in a 10x75 mm test tube. Add 1 mL of 0.2 M iodine solution. Add 0.5 mL of toluene, and agitate the test tube for a moment.
- Place about 1 mL of 0.1 M KF solution in a 10x75 mm test tube. Add 1 mL of 0.2 M iodine solution. Add 0.5 mL of toluene, and agitate the test tube for a moment. Has a reaction taken place?
- Perform the same reaction again, but this time using about 1 mL of 0.1 M KCl instead of the KF.
- Perform the same reaction again, but this time using about 1 mL of 0.1 M KBr solution.

Pre-Laboratory Questions: **Name________________**

Section________________ **Date_________________**

1. Find the formulas for the anhydride of each of the following acids. To obtain the formula of an anhydride, subtract H_2O's from the formula until all hydrogens have been subtracted. If the acid has an odd number of hydrogens, double its formula first.

   a. H_2SO_4

   b. NaOH

   c. $HClO_4$

   d. H_3PO_4

2. Determine the formula of the parent acid of each of the following anhydrides. To find the formula of the acid, add the indicated number of water molecules to the formula. Finally, divide through if the formula is divisible by some common factor.

of H_2O

   a. SO_2 (1)________________________

   b. N_2O_5 (1)________________________

   c. CO_2 (1)________________________

   d. P_4O_{10} (6)_________________________

3. Halogens and halides.
   a. Write Lewis dot structures for each of the halogen molecules, F_2, Cl_2, Br_2, and I_2.

   b. Based on the periodic trends, which of the halogen molecules do you expect to have the shortest bond?

   c. Based on periodic trends which halide ion, X^-, will be most stable, that is, lowest in energy? Briefly explain your reasoning.

Data and Results: **Name**____________________

Section _______________ **Date**_____________________

Solution	**Acidic or Basic?**	**Observations**
Sodium peroxide		
Calcium oxide		
Boron oxide		
Carbon dioxide		
Phosphorous pentoxide		
Sulfur dioxide		
Dichlorineheptoxide		

Reactions

Below are partial chemical equations describing the reactions of the oxides above. Based on your experimental results, add either H_3O^+ or OH^- as one of the products and then balance the chemical equation.

Sodium peroxide

$Na_2O_2(s)$ + ___$H_2O(l)$ $\rightarrow$ ___Na^+ (aq) + __O_2 (g) + ________

Calcium oxide

$CaO(s)$+ ___H_2O $(l)$$\rightarrow$ ___$Ca^{2+}(aq)$ + ________

Boron oxide

B_2O_3 (s) + ___H_2O (l) $\rightarrow$ ___$B(OH)_4^-$$(aq)$+ ________

Carbon dioxide

CO_2 (g) + ___H_2O (l) $\rightarrow$ ___$HCO_3^-$$(aq)$+ ________

Phosphorous pentoxide

$P_4O_{10}(s)$ + ___H_2O (l) $\rightarrow$ ___$H_2PO_4^-$$(aq)$+ ________

Sulfur dioxide

SO_2 (g) + ___H_2O (l) $\rightarrow$ ___$HSO_3^-$$(aq)$+ ________

Dichlorineheptoxide

Cl_2O_7 (l) + ___H_2O (l) $\rightarrow$ ___$ClO_4^-$$(aq)$ + ________

Part B: Preparation and Reactions of the Halogens

1. Observations for preparation of chlorine

2. Record the color of the toluene, **T**, and water, **W**, layers **after** mixing. Indicate the halogen that is in the toluene phase and the halide that is in the aqueous (water) phase. Compare your results using the potassium halide solutions (KF, KCl, KBr, or KI solution) to that of the control in order to determine whether a reaction has occurred.

		Control (Water)	KF	KCl	KBr	KI
Cl_2	T					
	W					
Br_2	T					
	W					
I_2	T					
	W					

Post-laboratory Questions: **Name**___________________

Section_______________ **Date**____________________

1. Based on your experimental results, what general trend can be observed for the acidity or basicity of the oxides as one proceeds across a period on the Periodic Table?

2. Based on your experimental results, what conclusions can be drawn about the oxidizing ability of the elemental halogens? Do you have conclusive evidence for fluorine? If not, can it be predicted by determining a pattern? Explain.

3. Write a balanced chemical equation for the reaction of the halogens with the halides. Do this only for those cases where a chemical reaction was observed in Part B.

4. Why doesn't the table in Part B of the laboratory allow us to make entries for the reaction of Cl_2 with KCl?