Periodic Properties Laboratory: Hydrolysis of Metal and Nonmetal Oxides.

Submit your answers to the prelab questions to the instructor at the beginning of the laboratory. You will not be allowed to begin work without having done so. Please include printout from any calculations done using EXCEL or another program.

Objectives
After completing these exercises you will be able to use the periodic table and the concepts of chemical periodicity, electronegativity, and oxidation states to predict the stoichiometry and acid/base properties of binary oxides.

Goals
- Use the periodic table to determine the valence electron counts of the elements.
- Understand periodic trends in electronegativity.
- Predict the type of bond that forms between two elements.
- To understand hydration/dehydration reactions of oxides.
- Predict the acid/base behavior of binary oxides upon hydrolysis.

Lab Summary
You will prepare samples of four binary oxide compounds for a hydrolysis reaction. You will determine the acid/base nature of the hydrolysis product using indicator solutions. You will examine your results to infer general principles that can be used to predict the acid/base behavior of binary oxides upon hydrolysis.

Prelab Background
The Periodic Table
The periodic table is far more than a mere list of elements by atomic number. Its organization into horizontal periods and vertical groups communicates information about the electronic structure of the atoms. As you move along a period of the table from left to right the number of electrons in the outermost shell or principle quantum level increases by one from element to element. The same increase in electron population occurs across all the periods but the valence electrons are being placed into different quantum levels. Elements in the same group or column possess the same number of valence electrons and they will also tend to become ions with the same charge. For the main group elements, those elements that are found in the s & p blocks of the periodic table, the group number equals the number of valence electrons. Thus, the electronic configuration of their valence shell is ns^xnp^y, where x (the number of electrons in the valence level s orbital) + y (the number of electrons in the valence level p orbitals) equals the group number and n is the number of the valence quantum level. The value of x equals 1 for group 1A and equals 2 for all other groups. The value of y progresses from a value of 1 for group 3A to a value of 6 for group 8. For example, the elements of group 3A all have 3 valence electrons and the electron configuration ns^2np^1. The chemical properties of the different elements are essentially determined by the outermost or valence electron count and therefore vary in a similar fashion across each period. This similarity between the periods gives the periodic table its predictive powers.

Bonding & Periodic Properties
Two useful applications of chemical periodicity are in determining the nature of bonding in a compound
and the compound stoichiometry. Stoichiometry is the study of the ratios and proportions of quantities in chemical reactions and compounds. In order to make use of chemical periodicity this we must consider the concept of electronegativity (EN).

Electronegativity is a measure of the ability of an element to attract or pull bonding electrons to itself. Electronegativity values vary across the periodic table in roughly predictable trends. These trends are: 1) EN decreases as you go down a column and 2) EN increases as you go across a row from left to right. The actual values of electronegativity of the elements are shown on the periodic table below. Fluorine (EN = 3.98) and oxygen (EN = 3.44) are the most electronegative elements; atoms of these two elements strongly pull on electrons. This is in agreement with our two trends as these elements are at the top of their respective groups and are on the right side of their row.

Pauling Electronegativity Scale

One view of bonding is that it is the sharing of electrons between two atoms. Electronegativity differences between two atoms that are bonded together results in an unequal sharing of electrons by the two atoms. The atoms can be thought of as having a tug-of-war over the electrons. When the difference between the electronegativities (ΔEN) of the two atoms is large enough the two atoms will ionize as the more electronegative atom totally removes an electron from the less electronegative atom. The more electronegative atom becomes an anion or negatively charged ion from the gain of an electron, while the less electronegative atom becomes a cation or positively charged ion as a result of the loss of an electron. Compounds made out of elements with a large ΔEN are called ionic solids. A property of ionic solids is that they tend to be soluble in polar solvents such as water. On dissolving ionic solids form aqueous cations and anions that are free to move in solution. Solid sodium hydroxide (NaOH) produces sodium ions (Na⁺) and hydroxide ions (HO⁻) in aqueous solution.

\[
\text{NaOH}_{\text{solid}} \rightarrow \text{Na}^+_{\text{aq}} + \text{HO}^-_{\text{aq}}
\]
With only a moderate difference in electronegativity between two elements a polar covalent bond will be formed that has the electrons shared unequally between the two atoms. Molecules with polar covalent bonds are called polar compounds. Polar compounds also tend to be soluble in polar solvents such as water but in comparison to ionic compounds, the polar compounds do not separate into ions.

Lastly, non-polar compounds are formed with covalent bonds that have electrons shared equally between the atoms. A true covalent bond is only formed between two atoms of the same element; since both atoms have the same EN, $\Delta EN = 0$ and the electrons are shared exactly equally. Bonds between atoms with a small $\Delta EN$ have electrons shared nearly equally. Hydrocarbons, compounds that are made up entirely of carbon and hydrogen, have a small $\Delta EN$ and are non-polar compounds. Hydrocarbons are also known as oils; as the saying goes “oil and water don’t mix”. Non-polar compounds are not soluble in polar solvents such as water.

<table>
<thead>
<tr>
<th>$\Delta EN$</th>
<th>Nature of Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt; 1.5$</td>
<td>Ionic Bond – Electrons are gained and lost by atoms</td>
</tr>
<tr>
<td>$1.5 &gt;$</td>
<td>Polar Covalent Bond – Electrons are shared unequally</td>
</tr>
<tr>
<td>$0.5 &gt;$</td>
<td>Covalent Bond – Electrons are shared equally</td>
</tr>
</tbody>
</table>

The periodic table helps to predict the number as well as the nature of the bonds that are formed in a compound. S & P block elements want to have a valence shell with 8 electrons. The elements will lose, take or share electrons so that they have 8 valence electrons; this is known as the Octet Rule. The exception is hydrogen, which is satisfied with 2 valence shell electrons. Generally elements on the left hand side of the periodic table with small electronegativity values will lose electrons and elements on the right hand side of the periodic table will gain or share electrons in order to achieve a valence shell octet.

In this laboratory we will be investigating binary oxides, oxides that are composed of oxygen and one other element. The compound stoichiometry of the binary oxides depends upon the valence state of the two elements. The chemical behavior of the binary oxides, with respect to hydrolysis and the nature of the product formed (acid or base), depends upon the bonding, ionic, polar covalent or covalent, between the constituent elements.

**Hydrolysis Reactions**

Nearly all elements E form binary oxides compounds with formulas $E_aO_b$ where a and b are stoichiometric coefficients. These oxides upon treatment with water undergo “hydrolysis” reactions. In a hydrolysis reaction the oxide dissolves in water and a new compound forms that has added $H_2O$ to its formula. There are two types of hydrolysis reactions:

1. hydrolysis to give basic compounds $E(OH)_x$; and
2. hydrolysis to form oxoacids $H_yEO_z$.

Basic oxides ionize to form hydroxide ions and $E$ cations in solution. An example is the hydrolysis of lithium oxide, a material with ionic bonds.

$$Li_2O + H_2O \rightarrow 2 LiOH$$

Followed by ionization of the resulting hydroxide to produce lithium ions and hydroxide ions in solution.

$$LiOH \rightarrow Li^{+}_{(aq)} + OH^{-}_{(aq)}$$
The hydroxide ion that is produced by the hydrolysis reaction is a strong base. The hydroxide ion will “accept” a proton or hydrogen ion (H+) from solution to form a water molecule.

$\text{OH}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O}$

A base is defined as a molecule or ion that is a hydrogen ion acceptor (H$_\text{aq}^+$). Hydroxide ions are very strong bases.

The hydrolysis of sulfur trioxide, SO$_3$, a compound with polar covalent bonds produces an oxoacid.

$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

The oxoacid produced in the hydrolysis is sulfuric acid, H$_2$SO$_4$, and it will ionize in solution to produce free protons or hydrogen ions (H$^+$) and the sulfate anion.

$\text{H}_2\text{SO}_4 (\text{aq}) \rightarrow 2 \text{H}^+_\text{aq} + \text{SO}_4^{2-} (\text{aq})$

An acid is defined as a molecule or ion that produces hydrogen ions (H$_\text{aq}^+$) in solution.

**Acids, Bases and Electronegativity**

How can you determine from the reactants of the hydrolysis of a binary oxide whether the product will be acidic or basic? You need to know that acids are relatively electron poor with respect to the electronegativity of the elements that compose the acid and that bases are relatively electron rich with respect to the electronegativity of the elements that compose the base.

Let's analyze the hydrolysis of lithium oxide: Li$_2$O + H$_2$O $\rightarrow$ 2 LiOH.

Our product will always form a bond between the non-oxygen element in the binary oxide and the oxygen atom of the reacting water molecule. The nature of this bond can be elucidated using our knowledge of electronegativity, in this case the bond will be ionic as EN(Li) = 0.98 and EN(O) = 3.44 so that $\Delta$EN = 2.46 which is greater than 1.5. This means that the oxygen atom will take an electron away from the lithium atom (Li) to form a lithium ion (Li$^+$). As a result the oxygen atom will have an extra electron, becoming electron rich and attractive to hydrogen ions (H$^+$).

Let's analyze the hydrolysis of sulfur trioxide: SO$_3$ + H$_2$O $\rightarrow$ H$_2$SO$_4$.

Our product will always form a bond between the non-oxygen element in the binary oxide and the oxygen atom of the reacting water molecule. The nature of this bond can be elucidated using our knowledge of electronegativity, in this case the bond will be polar covalent as EN(S) = 2.58 and EN(O) = 3.44 so that $\Delta$EN = 0.86 which is less than 1.5 and more than 0.5. This means that the oxygen atom will have to share an electron with the sulfur atom (S) although the sharing is not equal. As a result the oxygen atom will not have a full extra electron, it will be relatively electron poor with respect to its large electronegativity. The oxygen atom in the hydrolysis product wants to get more electrons than it initially has and it does by taking electrons from a hydrogen atom (H) that it is bound to producing a hydrogen ion (H$^+$).

In this lab, BaO(s), CO$_2$(g), P$_4$O$_{10}$ and SO$_2$(g) will be dissolved in water and the solutions will be tested to see if they are acidic or basic. The acidity or basicity of these solutions will be probed through the use of universal indicator and phenolphthalein. The color of these indicator dyes changes with the availability of protons in solution: the color of the universal indicator gradually varies from red (acidic or lots of protons in solution) to yellow (neutral) to purple (basic or few protons in solution), whereas the color of phenolphthalein abruptly colorless (acidic) to purple (basic).
Prelab Questions
1) Which is the more electronegative element?
   a) F Cl Br
   b) Al Si P
   c) K Ca Rb
   d) C N Si

2) What type of bonds will form in these binary compounds?
   a) NaCl
   b) H₂O
   c) CH₄
   d) CO
   e) FAt

3) Carbon is in group 4. What type of bonds would you expect a carbon atom to form with an oxygen atom? Provide formulas for oxide compound(s) that should form.

4) Compare the difference in electronegativities and bonding in the binary oxides CaO and AsO₃ and predict the hydrolysis products.