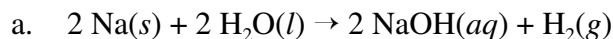


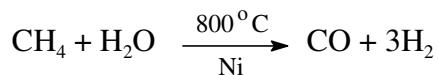
Name _____ Key _____

Chem 370 - Spring, 2018
Hour Exam III - Part 2
May 7, 2018

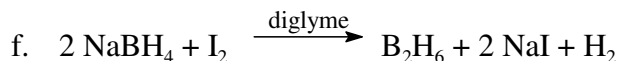
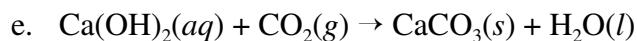
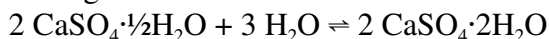
3. (40 points; 4 points each) In the spaces below the given information, write *balanced* chemical equations for **ten (10)** of the following. **Be sure to cross out the eight (8) you are not answering.**



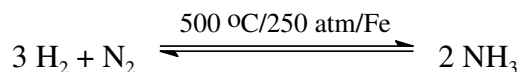
- c. Cracking of methane to produce hydrogen



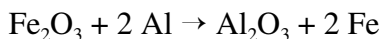
- d. Setting of Plaster of Paris



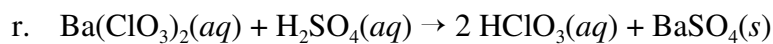
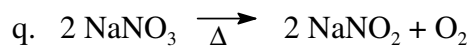
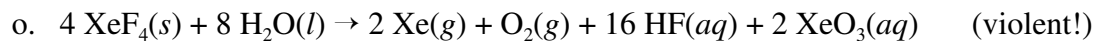
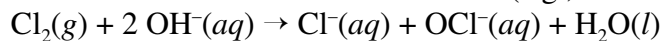
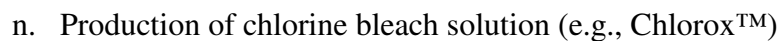
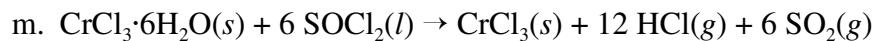
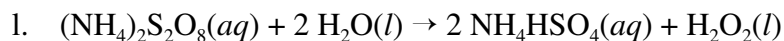
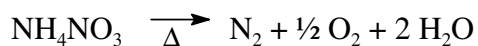
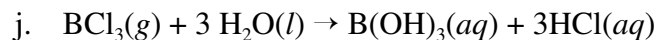
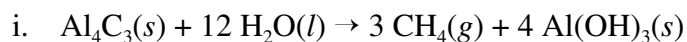
- g. The Haber process



- h. Goldschmidt or thermite reaction



Name _____ Key _____



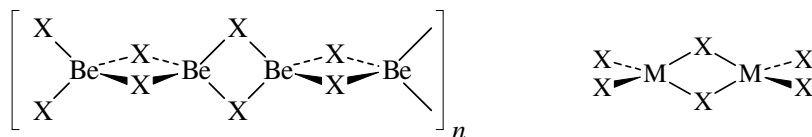
Name _____ Key _____

4. (16 points; 8 points each) Based on your knowledge of structure, reactivity, and bonding of the main group elements, offer *brief* chemical explanations for **two (2)** of the following four observations. **Be sure to cross out the two that you are not answering.**
- a. In Group 14 (IVA), the 2+ oxidation state becomes increasingly stable relative to the +4 state with increasing atomic weight. Explain why this trend occurs. What name is sometimes given to this tendency?

The stability of the bonds decreases rapidly down the group, but the ionization energy declines less rapidly. In the case of lead, the ionization energy to the +4 state is actually greater than that of tin. Therefore, the +2 state becomes increasingly favorable, because it requires less energy input for ionization. The tendency is sometimes called the "inert pair effect."

- b. In the solid, $\text{Be}(\text{CH}_3)_2$ and BeCl_2 bear a structural similarity to $\text{Al}_2(\text{CH}_3)_6$ and Al_2Cl_6 , respectively, inasmuch as all have bridging bonds. However, the nature of the bridge bonds differ among these molecules. Describe the structures (including sketches of the molecular structures), and the similarities and differences of the bonding in the bridge bonds.

All have tetrahedrally coordinated metal atoms (sp^3 hybridized) and bridge bonds. $\text{Be}(\text{CH}_3)_2$ and BeCl_2 are infinite chains, whereas $\text{Al}_2(\text{CH}_3)_6$ and Al_2Cl_6 are discrete dimers.



With CH_3 , the methyl radical contributes one electron, and the two metal atoms contribute a net of one additional electron in an sp^3 orbital to each bridge. This makes the bridge a $3c-2e$ bond; i.e., electron deficient. With Cl, the bridging Cl contributes three electrons from two p orbitals, and the two metal atoms contribute a net of one additional electron to each bridge. With Cl, the bridges are normal $2c-2e$ bonds for each M-Cl link.

Name _____ Key _____

- c. In our survey of the main group elements, we have seen that in each group the first element tends to show at least some chemistry that is distinct from the other members of its group. Give examples of first element uniqueness from at least three separate groups. What are the underlying causes of first element uniqueness and how do they result in this behavior?

[Many acceptable examples can be cited, too numerous to list here.] The main cause of first element uniqueness is high charge density. The Period 2 elements are the smallest in their groups, and therefore with their group characteristic oxidation states they have the highest charge density. Size alone limits the possible coordination to CN2-CN4. The heavier elements are often capable of CN5 or CN6. But more importantly, the charge density makes the compounds of first elements more covalent than the heavier members of each group. Where the heavier elements may form ionic compounds, the first elements show more covalent character, if not exclusively covalent bonding.

- d. The bond angles for the hydrides of the Group 15 (VA) elements are as follows: NH_3 , 107.8° ; PH_3 , 93.6° ; AsH_3 , 91.8° ; SbH_3 , 91.3° . Account for this trend. How does this trend affect the Lewis base strength of these compounds?

As the central atom becomes larger, the lone pair's influence on the geometry declines. The three hydrogen atoms maintain a relatively similar nonbonding separation in all cases, which is achieved with a smaller bond angle as the central atom becomes larger. The trend is consistent with Ligand Close Packing (LCP) considerations. In terms of VB modeling, the central atom's geometry is better explained with p orbital interaction with hydrogen s orbitals in the cases of PH_3 , AsH_3 , and SbH_3 , in contrast to sp^3 hybrids on N in NH_3 . This places the lone pair in a less directional ns orbital, making it less available for Lewis base donation. (In the MO model, a similar change in the distribution of the weakly bonding $\sigma(z)$ (a_1) MO occurs.) The consequence is that PH_3 , AsH_3 , and SbH_3 have little Lewis base tendency, in marked contrast to NH_3 , owing to the declining availability of the "lone pair".

Name _____ Key _____

Bonus Questions (4 points each)

- a. $[\text{Fe}(\text{CN})_6]^{3-}$ is bright red in color, but $[\text{FeF}_6]^{3-}$ is colorless. Explain the difference.

CN^- is a strong field ligand, and F^- is a weak field ligand. Thus, $[\text{Fe}(\text{CN})_6]^{3-}$ is a low spin d^5 configuration ($t_{2g}^5, ^2T_{2g}$), for which there are several spin-allowed transitions to excited states, giving rise to the red color. $[\text{FeF}_6]^{3-}$ is a high-spin d^5 configuration ($t_{2g}^3e_g^2, ^6A_{1g}$), for which there are no same-spin excited states and therefore no spin-allowed transitions. Only spin-forbidden transitions are possible, and their molar absorptivities are too low to give color that is perceptible.

- b. Briefly identify the hazards associated with the following:

Beryllium compounds

Extremely toxic, especially the dusts, which cause beryllicosis, a fatal lung condition.

Perchloric acid

Strong oxidant, which is explosive when concentrated to $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

Xenon trioxide

Shock sensitive explosive.

Hydrofluoric acid

Causes severe burns, which may not be initially painful, and can result in bone weakening.