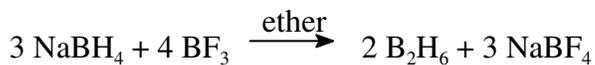
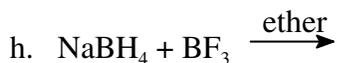
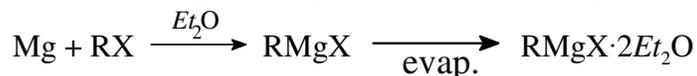
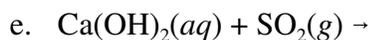
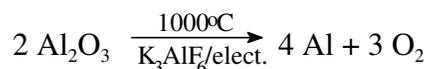
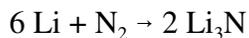
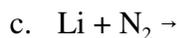
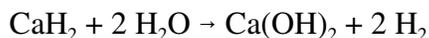
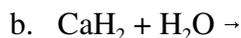
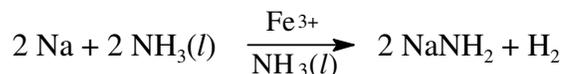
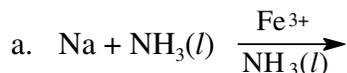


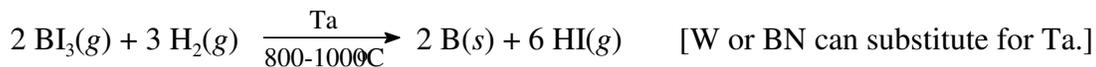
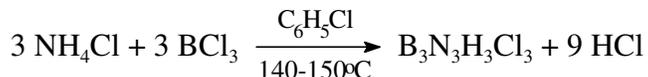
Name \_\_\_\_\_ Key \_\_\_\_\_

**Chem 370 - Spring, 2019**  
**Hour Exam III - Part 2**  
**May 13, 2019**

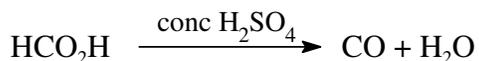
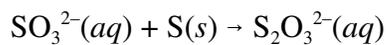
3. (40 points; 4 points each) In the spaces below the given information, write *balanced* chemical equations for **ten (10)** of the following. Indicate any conditions that are key to the reaction. **Be sure to cross out the eight (8) you are not answering.**



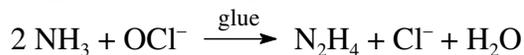
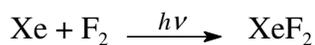
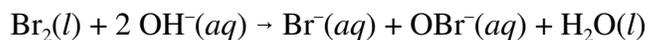
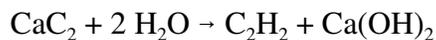
Name \_\_\_\_\_ Key \_\_\_\_\_

i. Obtaining high-purity boron from  $\text{BI}_3$ j. Synthesis of B-trichloroborazine,  $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ 

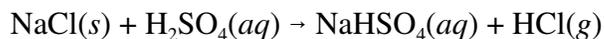
k. Non-explosive, low temperature decomposition of ammonium nitrate

l. Laboratory preparation of  $\text{CO}(g)$  from formic acidm.  $\text{SO}_3^{2-}(aq) + \text{S}(s) \rightarrow$ 

n. Raschig synthesis of hydrazine

o.  $\text{Xe} + \text{F}_2 \xrightarrow{h\nu}$ p.  $\text{Br}_2(l) + \text{OH}^-(aq) \rightarrow$ q.  $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow$ 

r. Industrial synthesis of hydrochloric acid



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 our survey of the main group elements, we have seen that diagonally related elements in periods 2 and 3 often show similar chemistries. What is the underlying cause of similar chemistry among diagonally related pairs of elements? Give at least three specific examples of uniquely similar chemistry among diagonally related elements.

**The main cause of unique chemistry among diagonally related pairs of elements is similarity of charge density. First elements, in general, tend to have more covalent character, owing to high charge density. Although larger, the diagonally related elements have higher charges, giving them similar charge density. Examples:**

**Li & Mg tend to form useful organometallic compounds**

**Be & Al form bridged species with either 2c-2e [e.g., BeCl<sub>2</sub>(s) & Al<sub>2</sub>Cl<sub>6</sub>] or 3c-2e bonds [e.g., BeH<sub>2</sub>(s) & Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>].**

**B & Si form borates and silicates with M-O bridging bonds, which facilitates their mixing in borosilicate glass.**

**[Many other examples can be cited.]**

- b. The group 13A stable ions in aqueous solution (Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Tl<sup>+</sup>) have the following reduction potentials for the half-reaction  $M^{n+} + ne^- \rightarrow M(s)$ .

Ion	Al <sup>3+</sup>	Ga <sup>3+</sup>	In <sup>3+</sup>	Tl <sup>+</sup>
$E^\circ$ (V)	-1.66	-0.549	-0.338	-0.336

By comparison, at pH 7,  $E = -0.42\text{V}$  for  $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$ . Explain why it is *not* possible to deposit aluminum metal at the cathode in an aqueous electrolysis, but it *is* possible to deposit gallium, indium, and thallium at the cathode in an electrolysis of aqueous solutions of their ions.

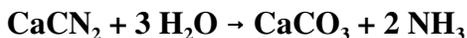
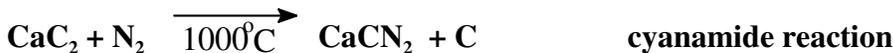
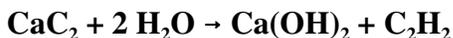
**The reduction potential for Al<sup>3+</sup> is too negative, relative to water's reduction, so H<sub>2</sub> would evolve at the cathode in an electrolysis of Al<sup>3+</sup> solutions. The reduction potentials for In<sup>3+</sup> and Tl<sup>+</sup> are favorable relative to water's reduction, and therefore their metals can be deposited in aqueous solution electrolysis. Ga<sup>3+</sup> would seem to be too negative for aqueous deposition, but a high overvoltage to H<sub>2</sub> formation at a Ga electrode makes it possible to deposit Ga metal by aqueous electrolysis.**

Name \_\_\_\_\_ Key \_\_\_\_\_

- c. The basis of organic chemistry is carbon's ability to catenate without limit. Why is carbon uniquely capable of limitless catenation? Why doesn't silicon show similar behavior? What is the more common bond type for Si, in lieu of homonuclear catenation? Why?

**The C-C bond strength is comparable to carbon's common heteronuclear bonds (e.g., C-H, C-O, C-Cl), which allows building of limitless chains that are stable relative to heteronuclear bonds. Moreover, carbon forms effective pπ-pπ bonds, resulting in double and triple bonds and π-delocalization. Larger silicon forms weaker homonuclear bonds than carbon, and the Si-Si bond is significantly inferior to heteronuclear bonds. The Si-O bond, which may be bridging, is more robust than the S-Si bond, and that is the ubiquitous bond type in silicon chemistry. Furthermore, silicon is too large to form strong π bonds or to establish π-delocalization.**

- d. The calcite cycle, which was developed long before the Twelve Principles of Green Chemistry, is a model of green chemistry. Show the five main reactions of this cycle and briefly explain what makes it so "green".



**The calcite cycle uses readily available raw materials (e.g., oyster shells) to make a variety of very useful products with no byproducts that are highly toxic (except CO) or that cannot be easily mitigated. Its principle waste product is CaCO<sub>3</sub>, which can be recycled in the first step.**

Name \_\_\_\_\_ Key \_\_\_\_\_

## Bonus Question (4 points)

- e. When sodium metal is burned in air, the principal product is a sodium-oxygen compound that is diamagnetic. When potassium is burned in air, the principal product is a potassium-oxygen compound that is paramagnetic. What are the two compounds, and why is one diamagnetic while the other is paramagnetic?

**The reactions are  $2 \text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$  and  $\text{K} + \text{O}_2 \rightarrow \text{KO}_2$ .  $\text{Na}_2\text{O}_2$  is sodium peroxide, which contains the  $\text{O}_2^{2-}$  ion.  $\text{KO}_2$  is potassium superoxide, which contains the  $\text{O}_2^-$  ion. The MO valence configuration of  $\text{O}_2^{2-}$  is  $\sigma(2p)^2\pi(2p)^4\pi^*(2p)^4$ , making it diamagnetic with a single bond. The valence configuration of the  $\text{O}_2^-$  ion is  $\sigma(2p)^2\pi(2p)^4\pi^*(2p)^3$ , making it paramagnetic with a bond order of  $1\frac{1}{2}$ .**