

HW 8 & 9
CHEM 362
Answer Key

Available: April 14, 2008

Due: April 21, 2008

Chapter 10

1. Why are alkali metals soft and volatile? Why are they called electropositive?

The softness and volatile nature of the alkali metals arises from the fact that the atoms only have one valence electron to share in the close packed structure resulting in a weaker interaction than in other metals.

They're called electropositive because the atoms readily lose their one electron to form cations. (This allows them to achieve noble gas configuration.)

2. What other ions have properties similar to alkali metals?

Ammonium (NH_4^+), Thallium (Tl^+) and Cobaltocenium ($[(\text{Cp})_2\text{Co}]^+$)



3. What are alkali solutions in liquid ammonia called?

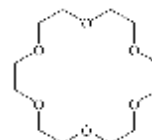
$\text{M}_{(\text{am})}$ (as opposed to $\text{M}_{(\text{aq})}$ for aqueous solutions)

4. Why is LiF almost insoluble in water whereas LiCl is soluble, not only in water, but in acetone?

LiCl has a significantly greater ionic nature than the more covalent LiF, and so it will more readily dissolve in polar solvents.

5. What is a crown ether? A cryptate?

A crown ether is a cyclic polyether (for ex. 18-crown-6)



A cryptate is a polycyclic aminopolyether. (for example 2,2,2-crypt)



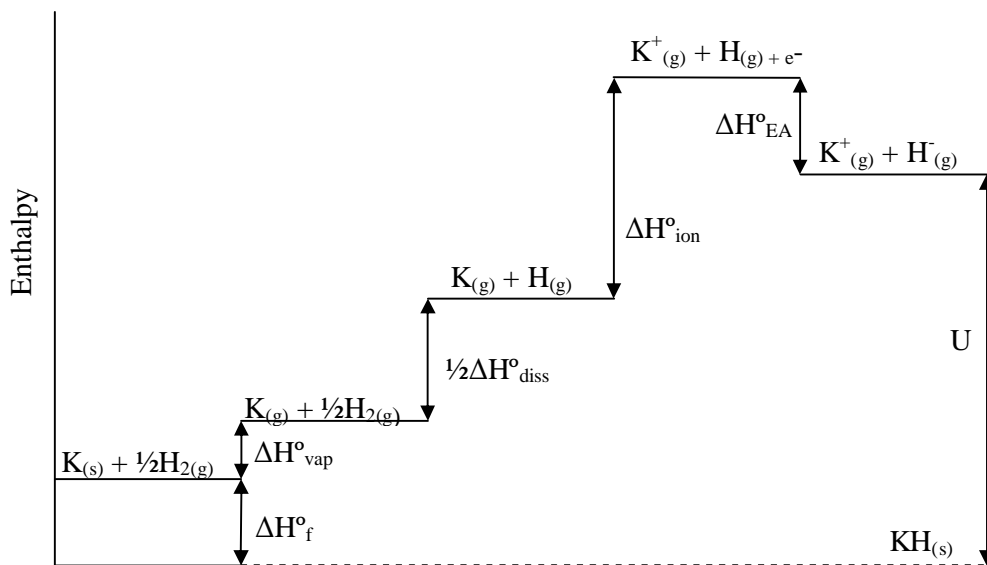
6. Anhydrous KOH in THF is one of the strongest known bases and will deprotonate exceedingly weak acids. Why? (Reactivity is related to solvation effects so consider the solvation of KOH by water versus THF).

While both water and THF will readily solvate the potassium hydroxide salt, ethers, such as THF are particularly good at solvating alkali metal cations. Water also forms a much stronger solvation sphere around the hydroxide anion due to hydrogen bonding. The hydrogen bonds will serve to lower the effective basicity of the hydroxide anion by stabilizing the anion and making it less accessible for reaction. THF is aprotic and thus cannot form hydrogen bonds. The interactions between hydroxide anion and THF are strictly electrostatic so the hydroxide is much more accessible for reaction, hence the strong basic character of hydroxide anions in THF.

7. Complete and balance the equations for the following reactions:

- $\text{KCl} + \text{Na} \rightarrow \text{NaCl} + \text{K}$
- $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$
- $\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 \rightarrow \text{NaO}_2 \text{ (with pressure)}$
- $\text{Cs} + \text{O}_2 \rightarrow \text{CsO}_2$
- $2\text{K} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C}_2\text{H}_5\text{OK} + \text{H}_2$
- $2\text{RbO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{RbOH} + 3\text{H}_2\text{O}_2$
- $\text{KOH} + \text{CO}_2 \rightarrow \text{KHCO}_3$
- $\text{C}_4\text{H}_9\text{Li} + \text{CH}_3\text{I} \rightarrow \text{C}_5\text{H}_{12} + \text{LiI}$
- $\text{K}^+ + \text{B}(\text{C}_6\text{H}_5)_4^- \rightarrow \text{KB}(\text{C}_6\text{H}_5)_4(\text{s})$

8. Write out a Born –Haber cycle for the formation of KH.

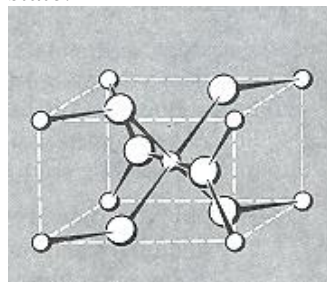
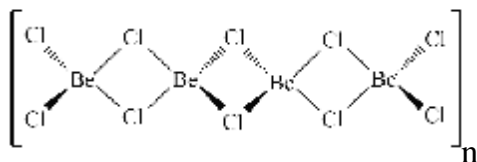


Chapter 11

9. Which compound, when dissolved in water, would give the most acidic solution, BeCl_2 or CaCl_2 and why?

BeCl_2 , a covalent compound and a good Lewis acid, is able to react with water to form $[\text{BeCl}_2(\text{OH})_2]^{2-}$ anions, liberating H^+ and creating acidic solutions. CaCl_2 on the other hand is strongly ionic and will form $\text{Ca}(\text{OH})_2$, which is a basic compound in water.

10. Draw the structures of BeCl_2 or CaCl_2 in the solid state.



**BeCl_2 exists as a polymer (above).
While CaCl_2 adopts the rutile structure (right).**

11. Why does linear X-Be-X exist only in the gas phase?

Beryllium dihalides will polymerize in the condensed phases to give saturated coordination of the beryllium atoms.

12. What is an important point about Beryllium compounds from a safety point of view?

Beryllium compounds are extremely toxic and are especially damaging to the lungs when inhaled.

13. Do the alkaline earth cations form many complexes? Which cations tend to do so and what are the best ligands (complexing agents)?

The alkaline earth cations do not form many complexes with the exception of “ Be^{2+} ”. Be^{2+} is capable of complexing with Lewis bases to form linear and tetrahedral compounds. Be prefers to bind with oxygen donors more so than nitrogen donors.

14. Why do the alkaline earths have higher melting points than the alkali metals?

The higher melting points exhibited by the alkaline earth metals, relative to the alkali metals, arise from two factors. The alkaline earth metals are smaller than the alkali metals (a result of increased effective nuclear charge). They also have two bonding electrons, instead of just one, resulting in stronger metallic bonds than those observed in the alkali metals.

15. Why does beryllium tend to form covalent compounds?

Beryllium's small size and high enthalpies of ionization and sublimation are responsible for the covalency observed in beryllium compounds. Neither the lattice or hydration energies of beryllium compounds are great enough to overcome these other factors and provide complete charge separation.

16. What are the main types of compounds formed by alkaline earth elements? Are they generally soluble in water?

The alkaline earth elements generally form ionic compounds which are soluble in water. The exception lies with Mg and especially Be which can form covalent compounds. This covalency decreases the solubility of the compounds of these two elements in water. An illustration of this point is that $\text{Be}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are slightly soluble in water while all other Group IIA hydroxides are strongly basic.

17. Finish the equations for the following reactions:

- a. $\text{BeCl}_2 + \text{Mg} \rightarrow \text{Be} + \text{MgCl}_2$
- b. $2\text{Be}(\text{s}) + \text{O}_2 \rightarrow (\text{with heat}) 2\text{BeO}$
- c. $\text{Be}(\text{s}) + \text{H}_2\text{O} \rightarrow \text{no reaction}$

18. Why do you think that the coordination numbers for Be^{2+} and Mg^{2+} are four and six respectively?

The small size of Beryllium prevents the complexation of six ligands around one metal center. Magnesium is larger and can accommodate the 2 extra ligands. Magnesium is a third row element and has empty 3d orbitals.