

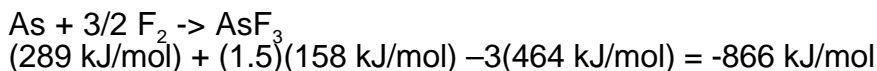
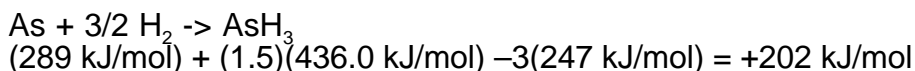
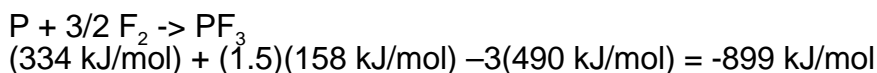
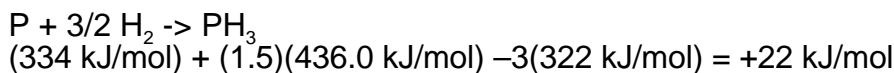
*CHE 514, Descriptive Inorganic Chemistry*  
*Spring, 2005*  
Problem Set 3 Key

Total points: 129 graduate students, 109 undergraduate students

**\*Questions 5 and 14 are optional for undergraduates.**

1. (10) MacKay 9.2

a. Heat of atomization is the energy needed to get P or As into the atomic state, analogous to breaking the N≡N bond.



b. Formation of the hydrides is slightly exothermic (N) or endothermic (P, As) because the H-H bond is stronger than the E-H bonds that are formed.

On the contrary, formation of the fluorides is moderately (N) to very exothermic (P, As) because the F-F bond is weaker than the E-F bonds that are formed.

2. (10) MacKay10.2 (ignore "and (b) the values for")

Decreasing mp and bp with increasing atomic mass is caused by the very weak metallic bonding of a single  $s^1$  bonding electron being spread over an increasingly large volume as the atomic volume increases.

bp (°C)  
Li 1342, Na 883, K 759, Rb 688, Cs 671

Same trend as melting point.

mp (°C)  
Be 1289, Mg 650, Ca 842, Sr 769, Ba 729, Ra 700

bp (°C)  
Be 2472, Mg 1090, Ca 1494, Sr 1382, Ba 1805, Ra (1700)

Similar trend to group 1 with Mg being anomalous in both mp and bp. The values are generally larger than group 1 values because there are twice as many metallic bonding electrons.

3. (10) Compare hydrogen bonds (protonic bridges) with the hydride bridges found in electron-deficient compounds. Be sure to contrast the geometries, number of nuclear centers, number of electrons, and give a specific example of each.

Hydrogen bonds (protonic bridges) consist of a hydrogen atom bridging two (or more) other atoms in a covalent bond, in which the hydrogen is less electronegative than the atoms to which it is bonded. These are 3-center 4-electron bonds. The E-H-E' geometry is usually linear. Typical example is HOH—OH'.

A hydride bridge consists of a hydrogen atom bridging two (or more) other atoms in a covalent bond in which the hydrogen is more electronegative than the atoms to which it is bonded. These are 3-center 2-electron bonds. The E—H—E' geometry is usually bent. A classic example is found in diborane, B<sub>2</sub>H<sub>6</sub>.

4. (5) Show the nuclear-spin microstates that comprise *ortho*- and *para*-hydrogen. In *ortho*-hydrogen molecules, the spins of the two hydrogen nuclei are parallel (quantum description of triplet,  $\alpha\alpha$ ,  $2^{-1/2}(\alpha\beta+\beta\alpha)$ ,  $\beta\beta$ ). In *para*-hydrogen molecules, the spins of the two hydrogen nuclei are opposite (quantum description of singlet,  $2^{-1/2}(\alpha\beta-\beta\alpha)$ ).
5. \*(10) Should nuclear-spin isomers of pure H-D exist? List the possible microstates. How they might divide up into states like *ortho* and *para*? (A qualitative answer is fine – no need for a complete quantum mechanical description.)

Because D has a nuclear spin of 1, it can have quantum numbers -1, 0, +1  
Therefore there should be six microstates that break up into a doublet and quartet.

(H quantum number)(D quantum number), S:

Four of the microstates, I think these four, comprise the quartet

(+1/2)(+1), +3/2

(+1/2)(-1), -1/2

(-1/2)(+1), -3/2

(-1/2)(-1), -3/2

Two of the microstates, I think these two, comprise the doublet

(+1/2)(0), +1/2

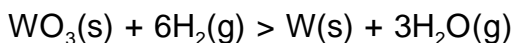
(-1/2)(0), -1/2

There is no S = 0 (NMR silent) form like *para*-H<sub>2</sub>.

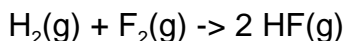
A brief literature search didn't turn up any information about the relative stabilities of the nuclear spin isomers. Possibly the HD nuclear spin isomers cannot be (or at least never have been) separated. Probably the energy differences between states are smaller and the interconversions between states are more facile because the two atoms in the molecule are not identical. The nuclear spin states should at least show up in the spectra (NMR, electronic, etc.) of HD.

6. (24) Write chemical equations for these reactions. (Some common trivial names are used intentionally.)

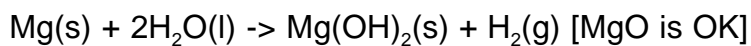
a. Tungsten (VI) oxide and hydrogen



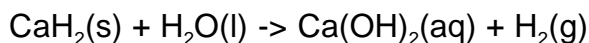
b. Hydrogen and fluorine



c. Magnesium and hot water



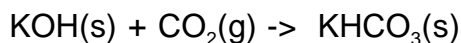
d. Calcium hydride and water



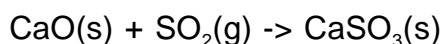
e. Cesium and dry dioxygen



f. Lye and carbon dioxide



g. Quicklime and sulfur dioxide



h. Baking soda upon heating



7. (15) Does each of these elements form an ionic, metallic or covalent hydride, or no stable hydride at all?

- a. ruthenium; none
- b. palladium;  $\text{PhH}_{<1}$ , metallic
- c. silver; none
- d. phosphorus;  $\text{PH}_3$  (and others), covalent
- e. calcium.  $\text{CaH}_2$ , ionic

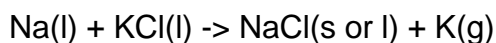
8. (5) Why is sodium hydroxide more water-soluble than sodium chloride?

From the solid-state side, NaCl has a higher lattice enthalpy than NaOH.

From the solution side, hydroxide ion forms hydrogen bonds with the solvating water molecules, whereas chloride only has ion-dipole attractions (or very weak hydrogen bonds).

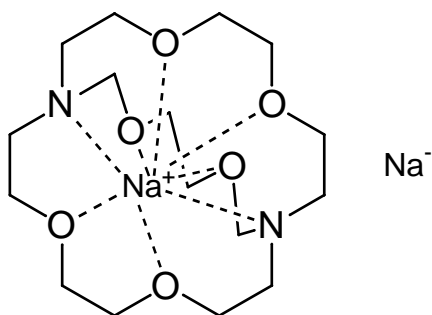
9. (5) Why is it possible to reduce potassium chloride to potassium by using sodium metal?

Potassium is a stronger reductant than sodium, so the reaction must be run under conditions where the more volatile potassium (bp Na 883 °C, K 759 C) distills from the reaction mixture, driving the unfavorable reaction



to the right.

10. (5) Sketch the structure of  $\text{Na}_2\text{Crypt}[2,2,2]$ .



11. (5) Why is calcium nitrate more water-soluble than calcium sulfate?

$\text{CaSO}_4$  has a higher lattice enthalpy than  $\text{CaNO}_3$  because of strong attractive forces between the  $2+$  and  $2-$  ions and good ion size match. The hydration enthalpy of three ions for  $\text{CaNO}_3$  is higher than two ions for  $\text{CaSO}_4$ , and there is an entropic advantage to releasing a larger number of ions.

12. (5) Why is the dissolution of anhydrous magnesium chloride in water more exothermic than the dissolution of magnesium chloride hexahydrate?

The major cause of the exothermicity of the dissolving of anhydrous magnesium chloride is the hydration of magnesium ion, with its high charge density. The hexahydrate  $[\text{Mg}(\text{OH}_2)_6]^{2+}(\text{Cl}^-)_2$  already contains the hydrated ion, so this step is missing from the enthalpy cycle.

13. (10) Why are organometallic compounds of lithium and magnesium more commonly used in organic synthesis than those of potassium and calcium?

Because of the higher charge to size ratio of  $\text{Li}^+$  and  $\text{Mg}^{2+}$ , their organometallic compounds are much more covalent, and therefore much more soluble in organic solvents.

14. \*(10) Treatment of  $\text{M}(\text{OH})_2$  or  $\text{MO}$  ( $\text{M} = \text{alkaline earth}$ ) with a carboxylic acid gives *volatile* carboxylates for  $\text{M} = \text{Be}$ , but involatile compounds for the heavier alkaline earths. Explain why the compounds are so different in properties.

$\text{BeO}$  is unique in forming the "basic carboxylates"  $\text{Be}_4\text{O}(\text{RCO}_2)_6$  (below), which are quite covalent because of the high charge to size ratio of  $\text{Be}^{2+}$ . The other alkaline earths are larger, preferring 6-coordination (or higher), so the 4-coordinate basic carboxylate structure is not favorable. Instead, they form normal carboxylates  $\text{M}(\text{RCO}_2)_2$  with three-dimensional, more ionic lattices.

