Chemistry 448/548 Key 3 Fall 2014

Very Short Answer Questions: (3 points each)

1/2. B_5H_9 is called pentaborane(9) and has a nido structure.

3. $B_2H_6 + xH_2O \rightarrow B(OH)_3$
4. A defect caused by missing ions from the lattice is called a Schottky defect defect.
5. An intrinsic semiconductor conducts electricity when heated.
6. Surface tension is directly proportional to the strength of intermolecular forces.
7. Those elements that hydrogen bond do so because of a combination of two factors: their small size and high electronegativity.
8. The tetrahedral ligand field stabilization energy for a d^1 metal is 0.6Δ Δ_T.
9. The *d*-electron configuration in $V(CO)_6$ is d^5.
10. What is the minimum number of electrons a stable, octahedral transition metal complex can be expected to have? 12

Discussion Questions: (You must show work to receive credit!)

1. What is doping in the context of seminconductors (be as specific as you can)? What kind of semiconductor is gallium doped into germanium? (6 points)

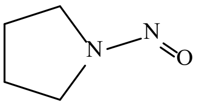
   The addition of a small, fixed amount of one substance to another to change the latter's properties is called doping. The dopant (added substance) is typically present around 1 ppm. Gallium in germanium is a *p*-type semiconductor.

2. Why is graphite a good conductor, while diamond is not? $(BN)_x$ forms a structure similar to graphite. What kind of conductor would it be and why? (10 points)

   Both forms of carbon exist as extended arrays, but graphite has an extended delocalized π-system through which electrons can travel, but diamond consists solely of localized σ-bonds. Since there is only one element, there is no additional barrier to electron flow.

   Boron nitride with a graphite structure is a semiconductor because there is an electronegativity difference between the elements. Because of this it costs energy to move electrons from the more electronegative nitrogen to the boron as electrons flow through the solid.

3. Crystals of the bis(N-nitrosopyrrolidine)hydrogen cation are typically prepared by evaporationg a solution of N-nitrosopyrrolidine and hexaflurophosporic acid (HPF_6). Explain why HPF_6 is employed as the acid instead of HF. (5 points)

   Crystals are generally more stable when cations and anions are near the same size because this allows for more efficient packing. Fluoride is a small anion and, obviously, smaller than PF_6^-. As a result, one obtains a more stable crystal lattice with the larger anion because it more nearly approximates the size of the cation.

4. List the intermolecular forces from strongest to weakest and provide the proportionalities/ratios for each (how the strength of each changes as a function of charge and distance). Explain why the one typically viewed as weakest may be considerably stronger than expected. (10 points)

   ion-ion – $E \propto Z^+Z^-/r$
   ion-dipole – $E \propto -|Z^+\mu^-|/r^2$
   dipole-dipole – $E \propto \mu^+\mu^-/r^3$

dipole-induced dipole – $E \propto Z\alpha/r^4$ or $E \propto \mu\alpha/r^6$
instanteous dipole-induced dipole – $E \propto \mu^+\mu^-/r^6$ (London dispersion forces)
London dispersion forces can be considerably stronger than expected because they depend on molecular size and polarizabilty. These factors depend, to a significant degree, on the number of electrons on the number of electrons (and shell they are in). In small atoms, the electrons are frequently controlled by their nuclei, but in larger atoms, the valence electrons are remote and more easily displaced.

5. What is the electroneutrality principle and discuss the physical processes that account for it? (10 points)

The electroneutrality principle tells us that the actual charges on species tend to be relatively small (usually between ±2). Two physical processes account for this.

The first is electronegativity. In metal complexes, there is technically a build-up of negative charge on the metal because ligands donate 2 e^- to the metal. These atoms are usually very electronegative causing sharing to be unequal. Thus the tendency is for the ligand to donate only a small portion of its e^- density.

The second is π-backbonding. Atoms that bind to metals frequently have vacant orbitals (p, σ^*, π^*) that the metal can transfer e^- density into from its *d*-orbitals. This is a feedback loop that effectively transfers e^- density back onto the ligand after it first donates it.

6. The bulk formulae of hydrates and clathrates on the surface look the same (e.g. $CaSO_4\bullet 2H_2O$). In fact, there are two kinds of hydrates. One kind is a subset of clathrates (i.e. clathrates with water as opposed to other molecules). An example of the other kind would be the coordination compound $[Cr(H_2O)_6]Cl_2$. How are they chemically different and why do clathrates form? (5 points)

The water molecule in a hydrate chemically bonds to the metal atom or ion, while in clathrates the water molecule simply occupies a hole in the crystal lattice. Clathrates form because there are holes in the lattice larger than the solvent molecules.

7. Which of the following would have the larger crystal field splitting energy (Δ_O)? Justify your answer. (10 points)

a) $PtCl_4$ (square planar) or $[PtCl_6]^{2-}$ - The difference is the presence of two more chloride ions. The extra four ligand electrons will repel the metal *d*-electrons and increase Δ_O.

b) $[Co(H_2O)_6]^{2+}$ or $[Co(H_2O)_6]^{3+}$ - Everything is the same except the oxidation state on the metal. The higher oxidation state will pull the ligands in closer which will increase the repulation between the metal *d* electrons and the ligand electrons resulting in a higher Δ_O.

8. Identify each element. (*Note*: Only 10 of the 11 elements are used.) (1½ point each)

V	It has the highest melting and boiling points of the first-row transition metals.
Cr	The high luster of this metal is noteworthy as is the colorful nature of its coordination compounds.
Ti	Its oxide has been used as both white paint pigment and smoke screen for ships.
Cu	A good electrical and thermal conductor that forms two historically important alloys.
Mn	Exhibits the widest range of oxidation states (11 in all) of any element and is the colorant in amethyst.
Ni	Corrosion resistant, ferromagnetic element that forms many industrially important alloys (e.g. Monel)
Co	Bluish metal which frequently forms coordination compounds.
Fe	It is found naturally in the minerals haematite and magnetite, among others.
U	Very dense; pyrophoric when finely divided.
Sc	Chemically very similar to aluminum. It has only one chemically important oxidation state.