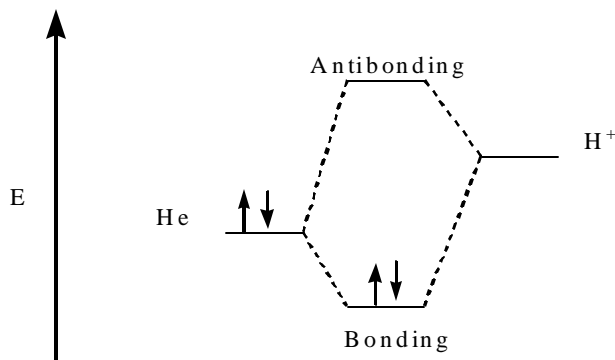


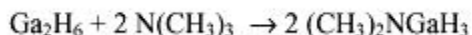
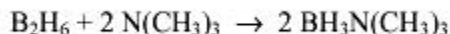
Chem 315, Fall 2000
Answers to Problem Set #7

- 8.3. a) See your textbook, chapter 3 (*bonding and MO theory*). All you have, is two electrons in your (HeH) + species.



- b) Which element is more electronegative: He ($2e^-$) is more electronegative, and in the formal sense the Mulliken electronegativity is much higher for helium (*for reference you can consult pp.30-31 of your textbook*). The more electronegative element the lower in energy it is making it contribute to the bonding orbital more.
- c) HeH⁺ seems to be unstable towards the proton transfer.

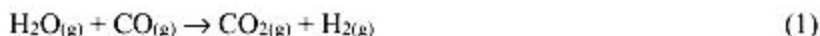
- 8.7. Borane, gallium hydride, aluminum hydride are tetrahedral in anionic state and trigonal pyramidal when neutral. Diborane, aluminum hydride and gallane are close relatives. All three act as Lewis acid (diborane is the strongest), which influences their reactions with TMA as follows:



(Or (CH₃)N.GaH₃), depending on the amount of reagents used).

- 10.2. a) *Not all* elements in this group are non-metals (typical examples of metallic components would include Al, Ga, In, Tl);
- b) There is a decrease in chemical hardness as you go down the group (Group XIII): boron and aluminum (chemically hard) are strong oxophiles and fluorophiles, as you go down the group, the heavier elements (Tl, Pb) are chemically softer and have a larger affinity for the soft anions;
- c) The Lewis acidity increases for BX₃ from X=F - to X=Br - because BF₃ is a very stable, and therefore, holds electrons more tightly (F - is a very hard ligand, strong π -bonding). Dealing with softer, less electronegative halogens, this stability decreases (weaker π -bonding), making the electrons more available, which increases the Lewis acidity;
- d) *Arachno*-boron hydrides have a $2(n+3)$ skeletal electron count. *Nido*- compounds are more stable. General trend is: the thermal stability of the *nido*-boranes is intermediate between this of *closo*- and *arachno*- boranes;
- e) Statement correct;
- f) The structures are different. First of all, the energy gap between the filled and empty π -bands is larger for BN, which apparently affects its conductivity and makes it an insulator. The difference in color is also self-evident (think, how these two are related). Next, in graphite, the carbon-hexagons are staggered, whereas in BN the hexagonal rings are stacked directly on top of each other, with boron and nitrogen atoms alternating in successive layers.

- 10.5. Most of the thermodynamic data can be found in your old Zumdahl's Chemistry book. Compare the two possible reactions:



	S^0 (1 bar), kJ/(K*mol)	ΔH_f^0 , kJ/mol	$\Delta G^0 - \Delta H^0 - T\Delta S^0$, kJ/mol
$\text{H}_2\text{O}_{(g)}$	188.84	-241.83	-298.1

$\text{CO}_{(g)}$	197.66	-110.52	-169.44
$\text{CO}_{2(g)}$	213.79	-393.51	-457.21
$\text{H}_{2(g)}$	130.68	0	-38.94
$\text{CH}_{4(g)}$	186.24	-74.87	-130.37

For rxn (1) $\Delta G^0 = -28.61$ kJ/mol (H_2); $\Delta S = -42.3$ kJ/(K*mole)

For rxn (2) $\Delta G^0 = 141.9$ kJ/mol (H_2); $\Delta S = 214.78$ kJ/(K*mole)

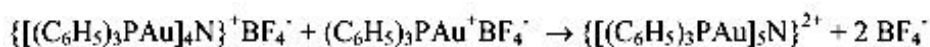
- b) rxn (1) is thermodynamically favorable, rxn (2) is NOT;
 c) i) high temperature would make the reaction (1) less favorable, and would make the reaction (2) more favorable. ii) high pressure would not affect the reaction (1), but would make the reaction (2) less favorable.

11.1. Tetrahedral P_4 molecule (see p.377 of your textbook for the detailed structure)

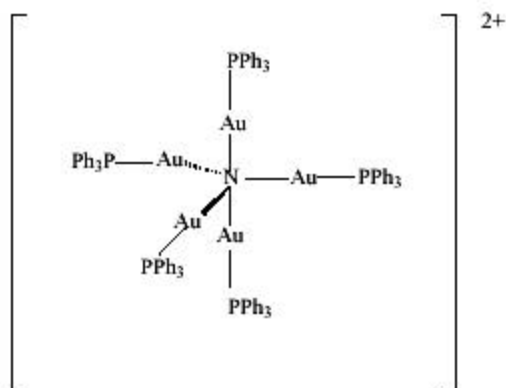
Total number of valence electrons: 20, 10 electron pairs. As you can see, each atom has a lone electron pair directed AWAY from the other atoms in the cluster, therefore we will have: $10 - 4 = 6$ electron pairs (12 skeletal electrons) for $n = 4$ atoms, which gives $(n + 2) = 6$ e - pairs, which corresponds to the *nido*- structure. A possible parental *closo*- structure would be P_4H .

11.5. The pentacoordinated nitrogen is possible. Just treat the nitrogen as you would treat a metal.

- a) synthesis (unbalanced reaction):



- b) Simplified structure (trigonal bipyramidal geometry):



- c) The fifth ligand is accepted to fill the MO in the electron-deficient created D_3H species. However the true description of such an unusual bonding is much more complicated, and is beyond the scope of this class.

11.7 a,b,c) No need to do the Huckel calculation. It is not in your book.

