

Very Short Answer Questions: (3 points each)

1. Ionic compounds are frequently soluble in high dielectric constant solvents.
2. Ions generally increase in size with increasing coordination number.
3. Be<sup>2+</sup> is the alkaline earth ion that polarizes best. (Be sure to write the ion.)
4. Nonbonding orbitals are orbitals with no net overlap.
5. Define electronegativity: The tendency of atoms in a molecule to draw electron density towards themselves.
6. The valence bond wave equation for HCl is:  $\psi = a\psi_{H(1)Cl(2)} + b\psi_{H(2)Cl(1)} + c\psi_{H(1)H(2)} + d\psi_{Cl(1)Cl(2)}$ . Order **a - d** according to size (use <, >, +): a = b > d > c or d > a = b > c
7. Bent bonds most typically occur in small, cyclic molecules.
8. What is the shape of SF<sub>4</sub>? butterfly or seesaw
9. Infrared spectroscopy operates on the 10<sup>-14</sup> - 10<sup>-16</sup> s<sup>-1</sup> time scale.
10. Two of the elements in Groups IVA - VIIA have only one isotope. What are they? fluorine and phosphorus

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

1. Explain why the Born-Landé equation ( $U = ANZ^+Z^-e^2/4\pi\epsilon_0r + NB/r^n$ ) is reasonable. (10 points)  
 There must be a term showing electrostatic attraction of cations to anions. This is the  $Z^+Z^-$  term. In addition to the electrostatic attraction, there must be a term to prevent the ions from approaching each other too closely, because ions occupy real volume and are not point charges. This is the last term which takes core  $e^-$  volume into account. From what you know about electrostatic attraction as charged bodies approach each other the level of interaction increases. This is consistent with the distance component of the equation being in the denominator. Since the material is in the solid phase and there are more interactions than simple the number of ions in the formula unit, a factor (A) must be introduced to account for multiple cation and anion interactions.
2. To ionize Mg to Mg<sup>2+</sup> costs two times as much energy as to form Mg<sup>+</sup>. The formation of O<sup>2-</sup> is endothermic rather than exothermic as for O<sup>-</sup>. Nevertheless, magnesium oxide is always formulated as Mg<sup>2+</sup>O<sup>2-</sup> rather than as Mg<sup>+</sup>O<sup>-</sup>. (5 points)
  - a) What theoretical reason can be given for the Mg<sup>2+</sup>O<sup>2-</sup> formulation.
  - b) What simple experiment could be performed to prove the magnesium oxide was not Mg<sup>+</sup>O<sup>-</sup>.
    - a) Mg<sup>2+</sup>O<sup>2-</sup> is favored because its lattice energy would be substantially larger than for Mg<sup>+</sup>O<sup>-</sup> (assuming the same lattice  $Z^+Z^-$  is 4 times larger).
    - b) Mg<sup>+</sup>O<sup>-</sup> would be paramagnetic, while Mg<sup>2+</sup>O<sup>2-</sup> would be diamagnetic so measure the magnetic susceptibility. Also, while not definitive, the reaction with H<sup>+</sup> should give you hydrogen peroxide for the former and water as the latter as products.

3. The bond angles in  $\text{NO}_2^+$ ,  $\text{NO}_2$ , and  $\text{NO}_2^-$  are  $180^\circ$ ,  $134^\circ$ , and  $115^\circ$ , respectively. Why? (10 points)

$\text{NO}_2$  and  $\text{NO}_2^-$  are  $sp^2$  hybridized with ideal ONO angles of  $120^\circ$ .  $\text{NO}_2$  has a single  $e^-$  in an orbital on N with 2 bonding pairs, while  $\text{NO}_2^-$  has a lone pair of  $e^-$  on N with two bonding pairs. Since lone pairs of  $e^-$  are larger than bonding pairs the ONO bond angle in  $\text{NO}_2^-$  should be compressed relative to the ideal  $120^\circ$ . This is observed ( $115^\circ$ ). An orbital with a single  $e^-$  should be smaller than one with two. This is because of reduced  $e^-e^-$  repulsions. Thus, the bond angle in  $\text{NO}_2$  should be larger than that in  $\text{NO}_2^-$ , which it is.

4. Compare and contrast X-ray, neutron, and electron diffraction methods. (10 points)

In X-ray diffraction a beam of X-rays is diffracted off the core  $e^-$  cloud of atoms in a small crystal. In neutron diffraction, neutrons are diffracted off the nuclei of atoms in a large crystal. Finally, in electron diffraction  $e^-$  are diffracted off  $e^-$  of atoms in gas phase molecules. An advantage of neutron diffraction over the other methods is that it allows hydrogen atoms to be found more easily.

5. What are the three types of phosphorus? Describe them. (10 points)

See handouts.

6. Consider the square planar molecule  $MH_4$ . Using a group increment scheme, what are the 4 bonding and 4 anti-bonding MOs for this molecule. Ignore weighting factors. (15 points)

Hint(s):

Make the  $z$ -axis pass through  $M$  and be perpendicular to the plane of the paper.

There are 9 possible orbitals on  $M$  that must be considered for bonding  $4s$ ,  $4p_x$ ,  $4p_y$ ,  $4p_z$ ,  $3d_{z^2}$ ,  $3d_{x^2-y^2}$ ,  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$ . Not all of these orbitals will be used in bonding.

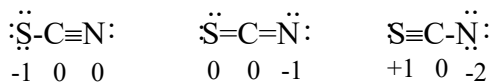
Draw the molecule and number the hydrogens 1-4 in cyclic fashion.

Draw the molecule with  $M$ - $H$  bond aligned along the coordinate axes,  $H_1 = +x$ ,  $H_2 = +y$ ,  $H_3 = -x$ , and  $H_4 = -y$ . Then  $4p_z$ ,  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$  cannot participate in bonding because they have no net interaction with the hydrogens.

<u>bonding</u>	<u>anti-bonding</u>
$\Psi = \Psi_{M(4s)} + (\Psi_{H1} + \Psi_{H2} + \Psi_{H3} + \Psi_{H4})$	$\Psi = \Psi_{M(4s)} - (\Psi_{H1} + \Psi_{H2} + \Psi_{H3} + \Psi_{H4})$
$\Psi = \Psi_{M(4p_x)} + (\Psi_{H1} - \Psi_{H3})$	$\Psi = \Psi_{M(4p_x)} - (\Psi_{H1} - \Psi_{H3})$ or
$\Psi = \Psi_{M(4p_y)} + (\Psi_{H2} - \Psi_{H4})$	$\Psi = \Psi_{M(4p_y)} + (\Psi_{H2} - \Psi_{H4})$ or
$\Psi = \Psi_{M(4p_x)} + \Psi_{M(4p_y)} + (\Psi_{H1} + \Psi_{H2} - \Psi_{H3} - \Psi_{H4})$	$\Psi = \Psi_{M(4p_x)} + \Psi_{M(4p_y)} -$ $(\Psi_{H1} + \Psi_{H2} - \Psi_{H3} - \Psi_{H4})$
$\Psi = \Psi_{M(3d_{x^2-y^2})} + (\Psi_{H1} + \Psi_{H2} - \Psi_{H3} - \Psi_{H4})$	$\Psi = \Psi_{M(3d_{x^2-y^2})} - (\Psi_{H1} + \Psi_{H2} - \Psi_{H3} - \Psi_{H4})$
$\Psi = \Psi_{M(3d_{z^2})} + (\Psi_{H1} + \Psi_{H2} + \Psi_{H3} + \Psi_{H4})$	$\Psi = \Psi_{M(3d_{z^2})} - (\Psi_{H1} + \Psi_{H2} + \Psi_{H3} + \Psi_{H4})$

7. Three possible resonance structures of  $SCN^-$  are (i)  $[S-C\equiv N]^-$ , (ii)  $[S=C=N]^-$ , and (iii)  $[S\equiv C-N]^-$ . Rank them in order of relative importance and justify your answer. (10 points)

The three structures are shown below with lone pair electrons and formal charges shown.



Structure (iii) is least important because it has the largest number of non-zero formal charges, they are non-adjacent, and a positive charge is placed on  $S$  which is more electronegative than  $C$ . Regardless of whether  $S$  or  $N$  is more electronegative, structure (i) is more important than structure (ii). This is because the  $p$  orbitals on  $C$  and  $N$  are about the same size and will overlap better than the  $p$  orbitals on  $S$  and  $C$ . Resonance form (i) has stronger bonds than form (ii).