

1. A Frenkel defect occurs when an ion is displaced from its normal site.
2. The Fermi level is highest filled molecular orbital in a band.
3. The filled collection of orbitals in a semiconductor is called the valence band.
4. Interstitial solvent molecules are solvent molecules that appear in gaps in the lattice.
5. What is the proportionality that corresponds to a dipole-dipole interaction? $E \propto \frac{\mu_1 \mu_2}{r^3}$
6. A ligand is a molecule, atom, or ion covalently bound to a metal center.
7. The barycenter is the average energy of a collection of orbitals. (e.g. the *d* orbitals in a complex)
8. Δ increases down a group.
9. $B_5H_9^-$ has a nido structure.
10. The bridging hydrogens in diborane(6) are attached to the boron via a 3-center-2-electron bond.

1. Write a short description of band theory. (5 points)

Atoms of a single element in a lattice are each surrounded by several other atoms. Thus, each atom has orbital overlaps with several other atoms. A Boltzmann (thermal) distribution of the atoms leads to a large number of different energies for each of the bonds between the atoms. For even relatively small masses of materials there are over 10^{20} atoms that give rise to a comparable number of bonds. Since these bonds are not all of the same energy a continuum of energy states is obtained and these are called bands. Two types of bands exist. The valence band is comprised of the bonding MO's and is filled while the conduction band is made up of the anti-bonding MO's and is nominally empty.

2. Would GaAs or InSb be a better semiconductor? Provide a physical justification for your answer. (10 points)

InSb is the better semiconductor. Two factors influence the conducting ability. The energy required to promote an electron from the valence band to the conduction band and the energy required to transfer an electron from one atom to its neighbor.

Both In and Sb have a higher energy valence shell than Ga and As. For this reason overlap is poorer and the energy gap between the valence and conduction bands is smaller. Likewise the electronegativity gap between In and Sb is smaller than that between Ga and As. Thus, there is a smaller barrier to moving electrons across a block of solid InSb because there is less tendency for the electrons to localize on one element.

3. List the following in order of increasing melting point H_2O , N_2 , LiCl, LiF, H_2 , He, BaO, $SiBr_4$, and SiO_2 . Justify your ordering. (16 points)

He, H_2 , N_2 , and $SiBr_4$ are nonpolar substances all held together only by London dispersion forces. These forces increase with increasing molecular volume so the order is as listed. H_2O is placed between N_2 and $SiBr_4$ because although it is smaller than both it is held together by hydrogen bonding which is fairly strong. It is placed in between because it is only a little smaller than N_2 so the hydrogen bonding overrides the size difference by the very much larger size of $SiBr_4$ more than compensates for the hydrogen bonding.

LiF, LiCl, and BaO are all held together by ionic bonding, while SiO₂ is a network covalent substance. The bonding here is much stronger than any of the intermolecular forces so all are solids at room temperature. Electrostatic attraction is proportional to Z^+Z^- so BaO has a higher melting point than either LiF or LiCl because of the higher charges on Ba (+2) and O (-2). LiF melts higher than LiCl because the latter has a more polarizable anion. Both F⁻ and Cl⁻ have the same charges, but Cl⁻ is larger. A more polarizable anion makes deforming the lattice and, hence melting the solid, easier. Finally, SiO₂ is a network covalent solid. These generally have extraordinarily high melting points because 4 stable covalent bonds must be broken.

4. Consider the linear complex: ML₂. Draw the ligand field splitting diagram for this molecule. Label the orbitals. Which *d*-electron configurations would undergo Jahn-Teller distortions? Neglect high/low spin considerations. (Hint: Assume the ligands are on the z-axis.) (10 points)

_____ points directly at incoming ligands and experiences the greatest e⁻-e⁻ repulsions
 z^2

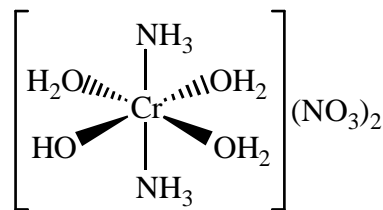
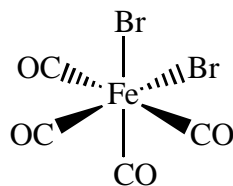
_____ _____ angled towards incoming ligands and experiences the intermediate e⁻-e⁻ repulsions
 xz yz

_____ _____ points away from incoming ligands and experiences the least e⁻-e⁻ repulsions
 xy x^2-y^2

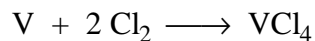
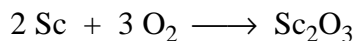
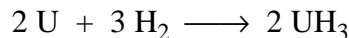
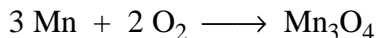
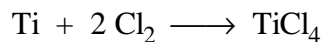
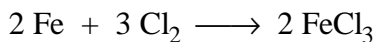
d^1, d^3, d^5, d^7

5. Write clear structural formulas for: (6 points)
mer, trans-diamminetriaquahydroxochromium(III) nitrate

cis-dibromotetracarbonyliron(II)



6. For 5 of the following 6 reactions: What are the products? Balance the equation. Clearly indicate the reaction you don't want graded. (15 points)



7. What is a catalyst precursor and why is it that in homogeneous catalysis catalyst precursors are added to reactions instead of the actual catalytically active species. (8 points)

A catalyst precursor is the material added to a reaction that then converts to the active catalyst. Catalyst precursors are used because the active catalyst is typically too reactive to isolate.