

1. Octahedral lattice holes are generally larger than tetrahedral lattice holes.
2. Core electrons are the major physical contributor to repulsion in the Born-Landé equation.
3. For a salt, decreased polarization results in higher melting temperatures.
4. In the equation: $\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \lambda\psi_{A(1)}\psi_{A(2)} + \lambda\psi_{B(1)}\psi_{B(2)}$, the final two terms account for ionic contributions to the wave function.
5. S and d atomic orbitals are typically gerade.
6. In general for resonance structures, formal charges on atoms should be minimized.
7. The interaction time in the diffraction methods is about 10^{-18} s.
8. The hybridization of a central atom in a molecule of square planar geometry is dsp^2 .
9. IF_3 is a T-shaped molecule.
10. The two elements that have a large number of allotropes are phosphorus and sulfur.

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

1. Compare and contrast carbon and silicon. (10 points)

Both are networked solids with atoms connected by covalent bonds at room temperature. Both have a form with the atoms in a diamond (sp^3) pattern, but carbon also has the graphite structure as well. Both have a very stable +4 oxidation state, but several other oxidation states are much more stable on carbon than silicon. Carbon readily forms π -bonds, while silicon does so with great difficulty. Carbon's two solid forms diamond and graphite are electrical insulators and conductors respectively, while silicon is a semiconductor.

2. Four (sets of) properties that characterize ionic solids were provided in the lecture. Name three and explain the basis of their origin. (10 points)

They are poor electrical conductors in the solid state, but conduct well when molten or in solution. This is because the ions are locked in place when in crystalline form while they can move (and carry charge) when in the liquid state or in solution.

They have high melting points. Ionic bonds are strong and omnidirectional. Since atoms are equally attracted to all anions around them, large amounts of thermal energy must be supplied to move them out of their lattice positions.

They tend to be hard and brittle. The same forces that keep the lattice from melting, keep it from being deformed. When deformation does occur, however, a shift of one position changes large numbers of attractive cation-anion interactions into repulsive cation-cation and anion-anion interactions and the crystal cleaves.

They are frequently soluble in high dielectric constant solvents. The collectively large number of dipole-ion interactions is frequently greater than the ion-ion interactions that exist in the crystal.

3. Discuss the bond angles in CH_2F_2 . What technique might be used to determine the angles and justify the method (briefly)? (10 points)

The idealized structure of CH_2F_2 is tetrahedral, but the angles are actually different from 109.5° . The fluorines are more electronegative than the hydrogens and will pull more electron density

towards themselves. *S* orbitals are more electronegative than *p* orbitals. Therefore, the hybrid orbitals on carbon binding to fluorine will contain more *p* character. This will cause the F-C-F bond angle to contract from 109.5°. The H-C-H angle will contain less *p*-character and will be expanded to greater than 109.5°. CH₂F₂ is a gas and so you would have to use electron diffraction to measure the angles.

4. Why is it conceptually reasonable for ΔH to be such a large negative (favorable number) for the lattice energy? (*Note*: A picture may be helpful in answering this question.)

In an ionic lattice each of the cations attracts all of the anions and is repelled by all of the other cations. The magnitude of the interactions decreases with increasing distance of separation of the interacting ions. In the end, the sum of the attractions exceeds that of the repulsions yielding a net attraction towards each ion in the crystal. The value is large because the result of these interactions is equivalent to more than an ionic bond to a nearest neighbor.

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

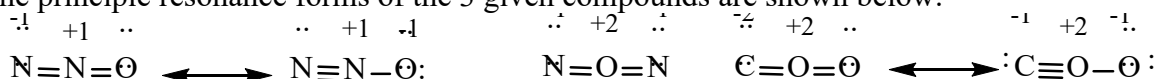
In X-ray diffraction a beam of X-rays are diffracted off the core e⁻ cloud of atoms in a small crystal. In neutron diffraction, neutrons are diffracted off the nuclei of atoms in a large crystal. Finally, in electron diffraction e⁻ are diffracted off e⁻ of atoms in gas phase molecules. An advantage of neutron diffraction over the other methods is that it allows hydrogen atoms to be found more easily because nuclei don't differ in size that much. X-ray diffraction has the advantage of working for small crystals, while electron diffraction works for volatile materials, but has lower accuracy.

6. Ferrocene is an unusually stable molecule. It is held together by bonds between the central iron atom and 10 carbon atoms. From organic chemistry, you know that many kinds of metal-carbon bonds are highly reactive (think Grignard or lithium reagents), yet ferrocene is not only air-stable but when you heated it to 170° it sublimed and didn't react either with atmospheric moisture. Why not? (5 points)

Ferrocene results from two kinds of bonding. The first is the ionic interaction that results from the attraction of an Fe²⁺ cation for the C₅H₅⁻ anion. The second is the chelate to all 5 carbon atoms on each ring. It is a covalent, interaction between all of the various orbitals on the metal with the π-system on the C₅H₅ ligand. In particular, the latter generates the high stability of the metal-carbon bonds.

7. The NNO molecule was discussed in the book. Would its isomer NON be more or less stable than NNO and explain your answer? Why does CO₂ have the structure it does instead of COO? (10 points)

The principle resonance forms of the 3 given compounds are shown below.



The NNO form is more stable than the NON form because the latter has the positive formal charge on the more electronegative element, a higher maximum formal charge, and more atoms carrying formal charges. The COO situation is even worse because OCO has no formal charges vs. 2 in the structure shown above and the charges are large and are placed opposite to electronegativity considerations.

