

Session #12: Homework Solutions

Problem #1

Silicon (Si) and chlorine (Cl) react with each other.

- What is the chemical formula of the reaction product?
- Do you expect the product to be a solid, a liquid, or a gas at room temperature? Rationalize your answer.

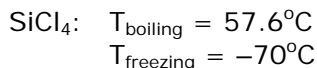
Solution

Silicon is a Group IV element like carbon (C) and will also exhibit sp^3 hybridization: 4 sp^3 orbitals with bonding angle = 109° . Unlike carbon, silicon cannot form double or triple bonds (by lateral p orbital overlap) because the atom is too large to permit lateral overlap.



Si is in the center of a tetrahedron with the chlorine atoms at the four corners.

- (b) $\Delta\chi = (\chi_{\text{Cl}} - \chi_{\text{Si}}) = 3.16 - 1.90 = 1.26$, which makes the compound SiCl_4 a covalent material (polar covalency). Since the bonding geometry is symmetric, the centers of fractional positive and negative charges coincide and the compound has no dipole moment. Intermolecular forces are therefore limited to London dispersion forces which are weak. It is expected that the material is a gas at room temperature. It could also be a liquid, but definitely not a solid.



Problem #2

Hydrogen (H) and sulfur (S) react with each other and form a compound.

- Give a reasonable chemical formula for the reaction product.
- Do you expect the molecule to be linear or not? If not, suggest a bond angle for the bonds between the reactant atoms.
- At room temperature do you expect the compound to be a solid, a liquid, or a gas? Rationalize your answer.

Solution

- Sulfur is a homologue of oxygen (O); both are in Group VI, so the valence shell has s^2p^4 configuration. There are two singly occupied p orbitals available for a σ bond formation with hydrogen, so the compound formed is: H_2S
- Assuming p-s orbital overlap on compound formation and the establishment of polar covalencies ($\Delta\chi = 0.38$), we anticipate that the (non-polarized and non-hybridized)

p–p bond angle is not 90° but likely more, and 100° appears a reasonable number. (It is frequently stated that the large bonding angle in H₂O and homologues can best be explained by involving sp³-type hybridization.)

- (c) The compound is expected to be a gas – not so much because of the smaller dipole moment compared to H₂O, but because of the absence of hydrogen bonding.

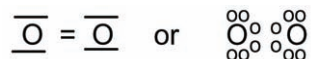
Problem #3

What types of bonds can be expected to be formed in each of the compounds listed below, and in what “state of aggregation” (gaseous, liquid or solid) are they encountered at room temperature?

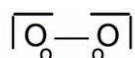
- (a) O₂
- (b) HCl
- (c) SiO₂
- (d) LiF
- (e) CH₄

Solution

- (a) O₂ is a gas at room temperature. It is customary to present the bonding as the formation of two unspecified covalent bonds:

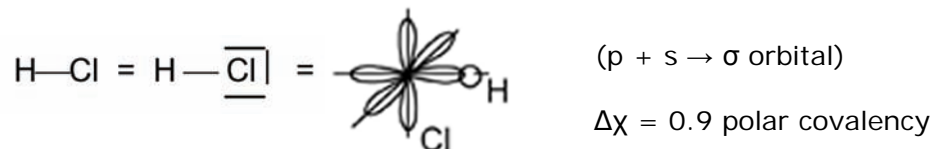


This presentation is, however, inconsistent with the observed paramagnetism which demands the existence of an unpaired electron – consequently it is now frequently rewritten as:

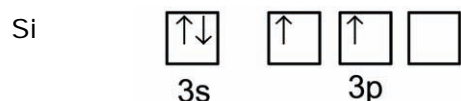


which in turn is not in line with the experimentally determined bond energy.

- (b) HCl is a gas at room temperature.

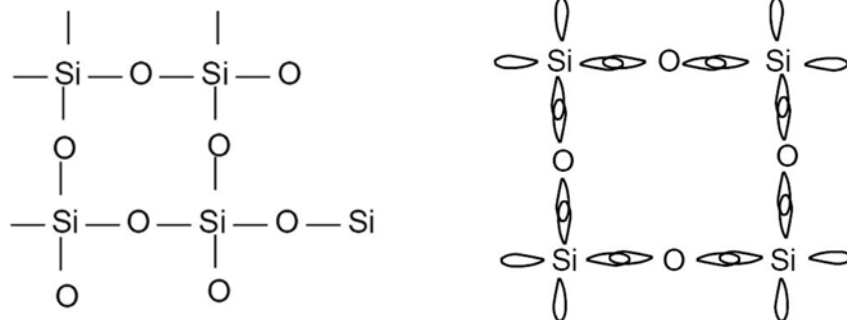


- (c) SiO₂ could be written as O=Si=O, but this would be incorrect!



Si, like C, is subject to sp³ hybridization and forms four equivalent hybrid orbitals directed with 109° bond angles at the corners of a tetrahedron. At each corner is located an oxygen atom which forms a bridge to another silicon with tetrahedral bond configuration – we obtain an ordered 3-dimensional structure.

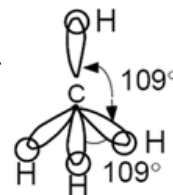
In planar presentation we would write:



The Si–O bond is a polar covalency with the Si-O-Si bond angle being stressed out of their 90° (p) configuration. SiO_2 is a solid at room temperature. (Your answer is acceptable if you say sp^3 hybridization leading to polar covalency.)

(d) Electron transfer and ionic bond formation: Li^+F^- . We have the formation of a solid at room temperature.

(e) CH_4 has sp^3 hybridization, forming a tetrahedron with 109° bond angles. The four σ bonds are polarized. CH_4 is a gas at room temperature.

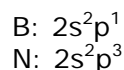


Problem #4

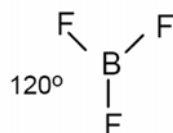
One of the two compounds, NH_3 or BF_3 , is found to exhibit a permanent dipole moment. Identify the polar species and account for the different bonding characteristics of the two species. Make appropriate sketches of the respective bonding configurations.

Solution

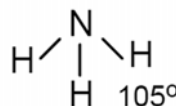
The answer to this question is found by looking at the valence shell configurations:



We realize that boron can hybridize into a planar sp^2 bonding configuration and form three σ bonds with fluorine. The compound is expected to be internally polarized, but no permanent dipole will thus result because of the bonding symmetry. Nitrogen has three singly occupied 2p orbitals directed at right angles to each other. Upon σ bond formation in NH_3 , we anticipate a pyramidal configuration with nitrogen at the apex. Because of bond polarization ($\Delta\chi = 0.82$), mutual repulsion of the activated hydrogen atoms is anticipated to increase the bond angle (which is found to be 105°). In fact, the large bond angle observed in NH_3 suggests sp^3 hybridization similar to that invoked in H_2O . In either case, the resulting molecule will exhibit a permanent dipole moment.



planar, non-polar



sp^3 hybridization, polar

Problem #5

Account for the following fact: H_2O and HF have much higher boiling points (100°C and 19.4°C respectively) than their homologues, H_2S and HCl (-60.7°C and -85°C), although the molecular weight of H_2O and HF is lower than that of H_2S and HCl .

Solution

Because O and F are more electronegative than S and Cl, H_2O and HF form stronger hydrogen bonds than H_2S and HCl . These strong hydrogen bonds increase the intermolecular forces enough in H_2O and HF to more than compensate for the higher weight of H_2S and HCl , and cause H_2O and HF to have significantly higher boiling points than their homologues.

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