

Solution to Selected Questions in Chapter #4

7. sp - linear



sp^2 - trigonal planar



sp^3 - tetrahedral



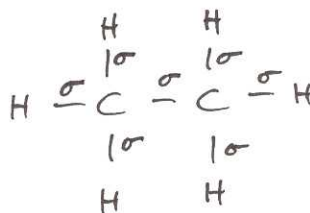
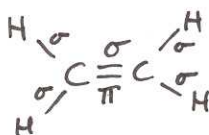
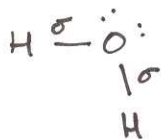
9. Sigma (σ) Bonds:

- composed of "s - type" electrons (formed from the overlap of s, sp , sp^2 , or sp^3 type orbitals)
- hard dense electron clouds
- very directional in nature (i.e. σ bonds and lone pairs of electrons determine molecular shape using the VSEPR theory)
- single bonds or the first bond in double or triple bonds

Pi (π) Bonds:

- composed of "p - type" electrons (formed from the overlap of p type orbitals)
- soft diffuse electron clouds that exist above and below a σ bond
- do not affect the directional nature of bonds
- the second bond in a double bond or the second and third bond in a triple bond

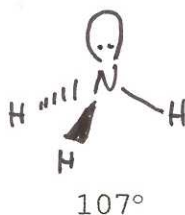
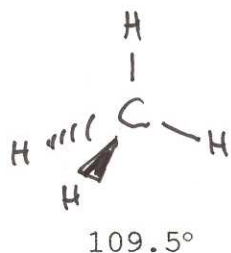
10.



14.

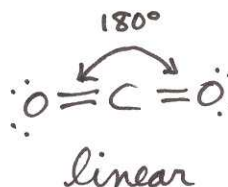
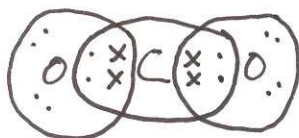
Formula	Base Shape	Actual Shape	Approx Bond Angle
HI	linear	linear	NA
BF ₃	trigonal planar	trigonal planar	120°
SiCl ₄	tetrahedral	tetrahedral	109.5°
CH ₄	tetrahedral	tetrahedral	109.5°
HCN	linear	linear	180°
OCl ₂	tetrahedral	angular	<109.5°
NH ₄ ¹⁺	tetrahedral	tetrahedral	109.5°
H ₂ O ₂	??	??	??

15. a)



b) The bond angles decrease as sigma bonds are replaced lone pairs. The electron density of a lone pair is greater closer to the central than is the electron density of a sigma bond. The reason for this is that the sigma bonding pair is stretch away from the nucleus in the act of bonding two positively charge nuclei together in a covalent bond. Since the lone pair has greater density closer to the central atom, it will produce a greater effect through the VSEPR Theory. Note that the bond angle in H₂S is 92°. This increase is a result of the greater diameter of the central sulphur atom which will allow the lone pairs to exert even more effect through the VSEPR Theory.

16. a) & b)



c) There are two ways to look at the polarity of carbon dioxide. The simplest way is to note that the bond polarization that exist between carbon (EN = 2.55) and oxygen (EN = 3.44) cancel out due to the linear shape of carbon dioxide creating a non-polar molecule. This does in fact happen to a great extent, however the difference in electronegativity causes both oxygens to steal electron density from the central carbon. This result in a δ^+ charge on carbon and δ^- charges on oxygen. Although this is not a true dipole, it is still possible to have a dipole like interaction between adjacent CO_2 molecules



17. a) N (EN = 3.04), Cl (EN = 3.16) therefore $\Delta\text{EN} = 0.12$

vs

C (EN = 2.55), Cl (EN = 3.16) therefore $\Delta\text{EN} = 0.61$

Based on ΔEN values alone, one would think that carbon tetrachloride would be considerably more polar than nitrogen trichloride. However the shape of the molecules has a major influence.

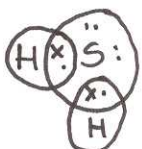


The tetrahedral arrangement of the CCl_4 causes bond polarizations to cancel out and this molecule is completely non-polar. NCl_3 on the other hand does have a net molecular polarization and is a true dipole molecule.

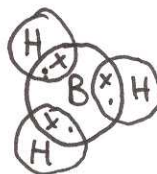
18. To best answer a) and b), draw Lewis dot diagrams and determine the shape first



linear



angular



trigonal planar



pyramidal

a) BeH_2 is linear (polarizations cancel out, therefore non-polar) while H_2S is angular and has a net molecular polarization (therefore polar).

b) BH_3 has 3 sigma bonds and no lone pairs, therefore trigonal planar shape, while NH_3 has 3 sigma bonds and one lone pair resulting in a tetrahedral base shape that truncates to a pyramidal shape

c) LiH is an ionic solid which will have a high M.P. since ionic intramolecular forces must be overcome to create a liquid. HF is a discrete covalent molecule with an intermolecular hydrogen bond. Only the intermolecular hydrogen bond need be overcome to create a liquid in this case. The intermolecular hydrogen bond is much weaker than the intramolecular ionic bond and therefore melting occurs at a lower temperature (lower thermal energy).

19. All three molecules have similar polarity. The difference is in the size of the molecules. As the molecules get larger, they contain more electrons etc. and therefore have stronger intermolecular van der Waals forces. Stronger intermolecular forces will increase the B.P.

20. NH_3 has the highest boiling point because the intermolecular force between ammonia molecules is a hydrogen bond, the strongest intermolecular force.

CH_4 and BF_3 both have van der Waals intermolecular forces. The van der Waals force for BF_3 is stronger (32 e^- total) than for CH_4 (10 e^- total). Therefore BF_3 has a higher B.P. than CH_4 .

21. a) Both M.P. are considered to be high. This is because both compounds are macromolecules held together by intramolecular forces. The metallic bond in nickel is stronger than the ionic bond in sodium chloride giving nickel the higher M.P.

b) NaCl will be non-conductive in the solid state because there are no free moving charged particles. Ni will readily conduct because free moving electrons in the solid metal can easily conduct a charge.

c) NaCl will dissolve well in water. Each ion will become hydrated by water (see diagram below). The hydration energy released in the hydration process is able to overcome the

lattice energy that holds the NaCl solid together in a crystal lattice. Ni like all metals is insoluble in water. The free moving electrons cannot be hydrated by water, therefore the lattice energy of a metal will always be far in excess of the hydration energy.

22.

Formula	Intramolecular Force	Intermolecular Force
$C_6H_{14}(l)$	covalent	van der Waals
$C_4H_9OH(l)$	covalent	hydrogen bond
$C_2H_5NH_2(l)$	covalent	hydrogen bond
$C_2H_5Cl(l)$	covalent	dipole interaction
$CaCO_3(s)^*$	covalent (within carbonate ion only)	ionic (between calcium and carbonate ions)
C_n (diamond)*	covalent	NA

* classified as macromolecules

23. pentane < diethyl ether < 1-butanol < butanoic acid

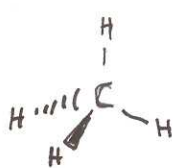
pentane: strictly non-polar, very poor interaction with water

diethyl ether: non-polar, however, the oxygen atom is able to accept a hydrogen bond from the hydrogen on water molecules, some interaction with water molecules

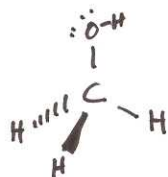
1-butanol: non-polar and polar regions, is able to fully hydrogen bond with water, the alcohol hydrogen can H-bond and the alcohol oxygen can accept an H-bond

butanoic acid: strongly polar and non-polar regions, the carboxylic acid group has a more strongly polarized hydrogen bond on the -OH group which can hydrogen bond better and there are two oxygens able to accept H-bonds

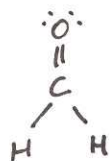
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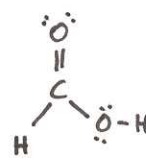
tetrahedral



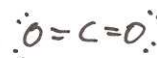
tetrahedral



trigonal
planar



trigonal
planar



linear

25. a) metallic: metallic ions and free moving electrons form a metallic intramolecular bond resulting in macromolecules

covalent network: neutral atoms held together by covalent bonds resulting in a macromolecule

The covalent bonds are somewhat stronger and much more directional than the metallic bonds. The resulting covalent crystal is harder and shatters when stressed. The metallic bonds are somewhat flexible allowing a metal to bend when stressed. Both types of bonding result in high M.P. compounds that are insoluble in water. The metallic bonding results in good electrical conduction due to free moving electrons.

b) covalent network: neutral atoms held together by covalent bonds resulting in a macromolecule

molecular: intramolecular covalent bonds between neutral atoms hold discrete molecules together which in turn are held to each other by intermolecular forces (van der Waals, dipole interaction or H-bond depending on the nature of the molecules)

The intermolecular forces responsible for making the molecular solids from discrete covalent molecules are considerably weaker than the intramolecular forces that hold covalent networks together. For this reason, the molecular solid is much softer and has a lower M.P. than the covalent network. The molecular solid may be soluble in several different solvents which can interact favourably through solvent solute intermolecular forces. The covalent networks will be insoluble in all solvents. Both types of compounds are non-conductive of a charge.

c) molecular: intramolecular covalent bonds between neutral atoms hold discrete molecules together which in turn are held to each other by intermolecular forces (van der Waals, dipole interaction or H-bond depending on the nature of the molecules)

ionic: oppositely charged ions are held together by strong intramolecular electrostatic forces of attraction

The intramolecular ionic bonds are much stronger than the intermolecular attractive forces that hold the molecular solid together. For this reason the ionic

solid will have a higher M.P. and will be harder than the molecular solid. The ionic solid may dissolve well in water since the ions can hydrate well. For the solubility of molecular solids see b).