Chapter 7

Lota_2, A1_Dæmi: Efnatengi og uppbygging sameindanna

The Ionic Bond

7.8 Why do nonmetals tend to form anions rather than cations?

ANS Cations tend to form from metals because most metals have relatively low first or second ionization energies. Chemically speaking, the pathway in which a metal loses one, two, or three electrons to form a "closed valence shell" cation is much preferred to one in which the metal must "capture" five, six, or seven electrons to fill an octet. For non-metals the process does not favor ionization of electrons (see the ionization energies); therefore, nonmetals are more likely to gain electrons and form anions.

7.10 Arrange the members of each of the following sets of cations in order of increasing ionic radii: (a) K^+, Ca^{2+}, Ga^{3+}, (b) Ca^{2+}, Be^{2+}, Ba^{2+}, Mg^{2+}, (c) Al^{3+}, Sr^{2+}, Rb^+, K^+, (d) K^+, Ca^{2+}, Rb^+

ANS (a) $Ga^{3+} < Ca^{2+} < K^+$ (b) $Be^{2+} < Mg^{2+} < Ca^{2+} < Ba^{2+}$

(c) $Al^{3+} < Sr^{2+} < K^+ < Rb^+$ (d) $Ca^{2+} < K^+ < Rb^+$

7.12 Which pair will form a compound with the larger lattice energy: Na and F or Mg and F? Why?

ANS The Mg with its +2 charge will form a compound with a higher lattice energy than NaF.

7.14 Use the concept of lattice energy to rationalize why sodium fluoride dissolves in water while calcium fluoride does not. Extending this reasoning, would you expect magnesium fluoride to be soluble?

ANS $CaF_{2\,(s)}$ formation releases a much larger amount of energy than does the formation of $NaF_{(s)}$ as a result of the higher charge on the calcium; therefore it stands to reason that more energy is required to disrupt the CaF_2 lattice which would translate into less solubility in water. Given the +2 charge on the Mg and the fact that the magnesium cation is about 75% smaller than the Na^+ ion, it would appear that the MgF_2 is insoluble in water for the same reason.

The Covalent Bond

7.16 Considering the potential energy of the interacting particles, how does covalent bonding lower the energy of the system?

ANS As the two atoms begin to approach one another the distance between them will shrink to the point that the electrons of one atom are attracted to the nucleus of the second and vice versa. This situation will result in a minimum energy.

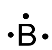
7.18 When a covalent bond forms, is energy absorbed or released? Explain how your answer is related to the graph you sketched in the previous problem.

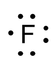
ANS The formation of a chemical bond always releases energy.

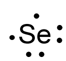
7.20 In terms of the strengths of the covalent bonds involved, why are combustion reactions exothermic?

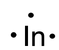
ANS The balance of breaking the C-H and O=O bonds and forming the C-O and H-O bonds results in energy being released from the system.

7.22 Draw the Lewis dot symbol for each of the following atoms. (a) boron (b) fluorine (c) selenium (d) indium

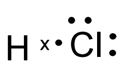
ANS (a) 

(b) 

(c) 

(d) 

7.24 Use Lewis dot symbols to explain why chlorine bonds with only one hydrogen atom.

ANS 

Chlorine only needs one more electron to reach an octet which can be achieved by making ONE bond with hydrogen.

7.26 How many electrons are shared between two atoms in (a) a single covalent bond, (b) a double covalent bond, and (c) a triple covalent bond?

ANS (a) 2 (b) 4 (c) 6

Electronegativity and Bond Polarity

7.28 How is electronegativity defined?

ANS Electronegativity is the attraction of an atom for the shared electrons in a covalent bond.

7.30 Certain elements in the periodic table shown in Figure 7.8 had no electronegativity value defined. Based on the definition of electronegativity and the identity of these elements, hypothesize as to why they have no electronegativity value.

ANS The noble gases are inert. With filled valence shells, there is no need to add further electrons to a noble gas. Those elements in listed in 6d without electronegativities are short-lived, recently discovered species. Perhaps the near future will hold more information on these species.

7.32 The bond in HF is said to be polar. For this to be true, the hydrogen atom must have less than one electron around it. Yet, the Lewis dot structure of HF attributes two electrons to hydrogen. Draw a picture of the electron density distribution for HF and use it to describe how the hydrogen atom can carry a partial positive charge. How can these two models of the HF bond (the electron density and the Lewis structure) seem so different and yet describe the same thing?

ANS The Lewis structure simply relates the fact that the H atom and F atom share a pair of electrons in a covalent bond. The Lewis structure does not address the electronegativity difference between the two atoms, but the electron density plot will show that the highly electronegative F atom has deeply influenced the "sharing" of this electron pair.

7.34 Based on the positions in the periodic table of the following pairs of elements, predict whether bonding between the two would be primarily ionic or covalent. Justify your answers. (a) Ca and Cl, (b) P and O, (c) Br and I, (d) Na and I, (e) Si and Br, (f) Ba and F.

ANS (a), (d), and (f) are ionic bonding. (b), (c), and (e) are examples of covalent bonding.

7.36 Considering the trends in electronegativity shown in Figure 7.8, explain why alloys that form between two or more transition metals are not ionic substances.

ANS With electronegativities ranging from 1.1 to 1.9, there is simply not enough difference in electronegativity to have ionic alloys.

7.38 Which of the following contains *both* ionic and covalent bonds in the same compound? (a) $BaCO_3$, (b) $MgCl_2$, (c) BaO, (d) H_2S, (e) SO_4^{2-}

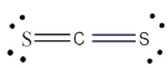
ANS (a) The barium cation is ionically bound to the carbonate anion. The "internal" bonds of the carbonate ion (i.e., C to O) are covalent though.

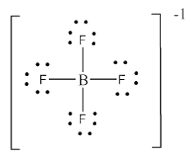
7.40 Suppose you wanted to make a diatomic molecule using two different halogen atoms. What combination of halogens would be the least polar?

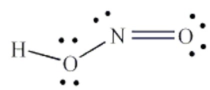
ANS Cl and Br would form the least polar diatomic molecule from this group.

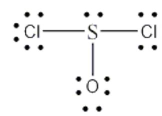
Keeping Track of Bonding: Lewis Structures

7.42 Draw a Lewis structure for each of the following molecules or ions: (a) CS_2, (b) BF_4^-, (c) HNO_2 (where the bonding is in the order HONO), (d) $OSCl_2$ (where S is the central atom)

ANS a) 

b) 

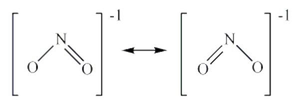
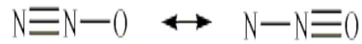
c) 

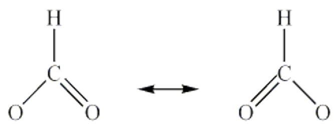
d) 

7.44 Why is it impossible for hydrogen to be the central atom in the Lewis structure of a polyatomic molecule?

ANS H can only form one bond. To be the central atom, H would have to form more than one bond in any non-binary molecule.

7.46 Draw resonance structures for (a) NO_2^-, (b) NNO, and (c) HCO_2^-.

ANS (a)  (b) 

(c) 

7.48 Draw the Lewis structure of two resonance forms for ozone, O_3. What prediction can you make about the relative lengths of the O-O bonds?

ANS Given that resonances do not exist as literal mixes of compounds but rather as a hybridization of the resonance forms, the two bonds should be equal in length. In other words there is not a mix of two compounds each having a single bond O-O and a double bond O=O. In fact, the situation more closely resembles one in which there is one type of molecule with a pair of equal bond lengths best described as a 1.5 bonds.

7.50 Consider the nitrogen–oxygen bond lengths in NO_2^+, NO_2^-, and NO_3^-. In which ion is the bond predicted to be longest? In which is it predicted to be the shortest? Explain briefly.

ANS The shortest bond belongs to NO_2^+ in which both N-O bonds are double bonds. This means that the bond order for this molecule is 2.0. The longest is the nitrate as the bond order is 1.33.

7.52 Identify what is incorrect in the Lewis structures show for BBr_3 and SO_2.

ANS (a). The central atom, B, has been assigned five valence electrons when it actually only has three.

(b). A molecule formed by two oxygen atoms and one sulfur atom have a total of 18 electrons. This representation uses twenty which is incorrect.

7.54 Chemical species are said to be *isoelectronic* if they have the same Lewis structure (regardless of charge). Consider these ions and write a Lewis structure for a neutral molecule that is isoelectronic with them. (a). CN^- (b). NH_4^+ (c). CO_3^{2-}

ANS (a). N_2; a triple bond between N atoms

(b). The ammonium cation would be isoelectronic with a neutral CH_4 molecule.

(c). SO_3

Orbital Overlap and Chemical Bonding

7.56 Distinguish between constructive and destructive interference.

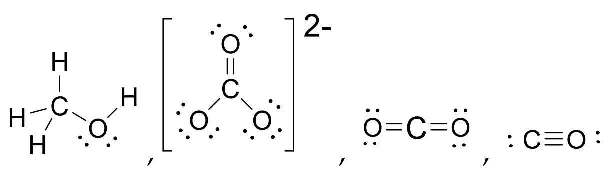
ANS Constructive interference occurs when two waves are exactly in phase with one another. The resulting wave will have twice the amplitude of either original. Destructive interference happens when the two waves sum but are not in phase. If this occurs, the crest of one wave will correspond to the valley of the other, and the two waves will cancel one another.

7.58 How does overlap explain the buildup of electron density between nuclei in a chemical bond?

ANS When a chemical bond is formed, there is an overlap of the wave functions of the two atoms. The overlap of these wavefunctions results in a marked increase in electron density in this region between the two nuclei.

7.60 CO, CO_2, CH_3OH, and CO_3^{2-} all contain carbon-oxygen bonds. Draw Lewis structures for these molecules and ions. Given that double bonds are stronger than single bonds, and triple bonds are stronger than double bonds, rank the four species in order of increasing C–O bond strength.

ANS $CH_3OH < CO_3^{2-} < CO_2 < CO$



7.62 Draw the Lewis dot structures of the following compounds and identify the number of pi bonds in each. (a). Cl_2O (b). H_2CCH_2 (c). HCCCN (d). SiO_2

ANS (a) zero, (b) one, (c) four, (d) two

Hybrid Orbitals

7.64 The number of hybrid orbitals formed must always be equal to the number of atomic orbitals combined. Suggest a reason why this must be true.

ANS According to the Pauli Exclusion Principle an orbital will contain two electrons with different m_s values. This holds true for each orbital whether or not it has been hybridized. For example, if three orbitals are hybridized together, the result will be three degenerate (equal energy) orbitals.

7.66 Considering only *s* and *p* atomic orbitals, list all the possible types of hybrid orbitals that can be used in the formation of (a) single bonds, (b) double bonds, and (c) triple bonds.

ANS a) single bonds = sp^3, sp^2, sp; double bonds = sp^2; triple bonds = sp

7.68 What type of hybridization would you expect for the carbon atom in each of the following species? (a) CO (b) CO_2 (c) H_2CO (d) CH_2F_2

ANS (a) sp; (b) sp; (c) sp^2; (d) sp^3

Shapes of Molecules

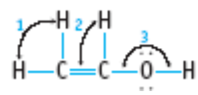
7.70 Predict the geometry of the following species: (a) SO_2, (b) $BeCl_2$, (c) $SeCl_4$, (d) PCl_5

ANS (a) bent, (b) linear, (c) see-saw, (d) trigonal bipyramidal

7.72 Predict the shape of each of the following molecules or ions. (a). PH_4^+ (b). OSF_4 (c). ClO_2^- (d). I_3^-

ANS (a) tetrahedral, (b) trigonal bipyramidal, (c) bent, (d) linear

7.74 Give approximate values for the indicated bond angles: (a) Cl—S—Cl in SCl_2, (b) N—N—O in N_2O, (c) bond angles 1, 2, and 3 in vinyl alcohol.



ANS (a) 109º (b) 180º (c) #1 - 120º, #2 - 120º, #3 - 109º

7.76 Describe why a central atom with four bonding pairs and one lone pair will have the lone pair in an equatorial rather than an axial location.

ANS This minimizes repulsion because the lone pair is 90º from two bound atoms rather than being 90º from three bound atoms.

Insight into Molecular Scale Engineering For Drug Delivery

7.78 Describe why treatments like chemotherapy for cancer patient often have serious side effects. What is a strategy that could lessen such side effects?

ANS The chemotherapeutics often attack healthy cells as well as the cancerous ones. If reagents could be developed to specifically attack the cancerous cells, the side effects may be mitigated or virtually eliminated. For further information on the topic, please refer to biomedical search engines and journal publications.

7.80 How does a MSN differ from amorphous silica so that it has improved biocompatibility?

ANS Mesoporous silica nanoparticles have honeycombed structures of SiO_4 units which results in enormous amounts of surface area inside the actual MSN particle. The pore size is smaller than a red blood cell, and this mitigates the damage that can be done compared to amorphous silica.

Additional Problems

7.82 In 1999, chemists working for the Air Force Research Laboratory reported that they had produced a compound containing an unusual ion with the formula N_5^+. This ion had not been expected to exist, and its instability makes it both difficult and dangerous to prepare.

Consider the possible Lewis structure below. Indicate the hybridization expected for each nitrogen atom and the expected bond angles.

Assuming the structure shown above is correct, how many of the five nitrogen atoms would *always* lie in the same plane?

ANS The hybridization goes from left to right: sp^2, sp, sp, sp, sp^2; all five would lie in the same plane. All bond angles should be 180 ^{o}

7.84 Consider the Lewis structure below. Is this an ion? If so, what is its charge?

ANS Yes it is an anion with a -1 charge.

7.86 Methyl cyanoacrylate, $C_5H_5NO_2$, is the compound commonly sold as super glue. The glue works through a process called polymerization, in which molecules of methyl cyanoacrylate form strong chemical bonds to one another and to the surfaces being glued. This process is initiated by traces of water on the surfaces. The skeletal arrangement of the atoms in methyl cyanoacrylate is shown below. Complete the Lewis structure of the compound by adding lone pairs of electrons or multiple bonds where appropriate. Using your Lewis structure, predict the hybridization for the six central atoms (the five carbon atoms and the leftmost oxygen atom). How many sigma bonds and how many pi bonds does your structure contain?

<u>ANS</u> The hybridization for the six atoms from left to right is: sp^3, sp^3, sp^2, sp^2, sp, sp. The hybridization for the carbon atom below the second carbon from the right is sp^2. The structure contains 12 sigma and four pi bonds (and five lone pairs of electrons). This agrees with the count of total valence electrons available being 42 electrons.

Focus on Problem Solving Exercises

7.88 Electrical engineers often use lithium niobate, $LiNbO_3$, in designs for surface acoustic wave filters in devices such as cellular phones. What type(s) of bonding would you expect to be present in this compound?

<u>ANS</u> The bond between Li and the niobate is ionic. The bonds between the niobium and oxygen within the niobate are covalent.

7.90 Another “grand challenge” for engineering is managing the nitrogen cycle. Use the nature of the chemical bond in diatomic nitrogen to explain why any management is needed for this biogeochemical cycle. With so much nitrogen available in the atmosphere, why are engineering solutions needed to manage nitrogen for agricultural uses?

ANS Elemental N_2 features a triple bond between two nitrogen atoms. Plants cannot use nitrogen in this form. They require “fixed” nitrogen such as that in NH_3 or NO_3^- where the oxidation number of the nitrogen is +5.

7.92 Both ozone, O_3, and oxygen, O_2, absorb UV light in the upper atmosphere. The ozone, however, absorbs slightly longer wavelengths of UV light – wavelengths that would otherwise reach the surface of the planet. (a). How can Lewis structures help explain the bonding difference between ozone and oxygen that gives rise to the difference in the absorption wavelength? (b). What relationship or relationships between light and energy do you need to know to understand this photochemical application of Lewis structures?

ANS a). The presence of an ozone resonance pair is easily seen with an attempt at drawing the Lewis structure. The resonance means that the pi-bond is "smeared" between the two O-O bonds in the ozone molecule, and this leads to a bond that is unlike the O=O bond of oxygen. With a different bond comes a different wave function and electron density, and this difference in character will result in a different absorption of uv light.

b) An understanding of wave properties and the duality of light would be helpful.

7.94 Hydrogen azide, HN_3, is a liquid that explodes violently when subjected to shock. In the HN_3 molecule one nitrogen-nitrogen bond length has been measured to be 112 pm and the other 124 pm. Draw a Lewis structure that accounts for these observations. Explain how your structure reflects these experimental facts.

ANS The three N atoms are held in a linear fashion by double bonding. The H is bonded to a lone pair of one of the terminal N atoms. This Lewis structure places opposite formal charges on two adjacent N atoms which results in the bond length differences.

Cumulative Problems

7.96 How does electronegativity relate to the periodic trends of atomic properties? How does effective nuclear charge, the concept invoked to understand those trends, also help explain the trends in electronegativity?

ANS Electronegativity increases from left to right across a period and increases from bottom to top in a group or family of elements, the same trends seen for size, ionization energy, etc. Effective nuclear charge illustrates the differences in the attractive forces between valence electrons and increasing nuclear charge as one moves across a period from left to right.

7.98 Use Lewis symbols to describe how free radical polymerization occurs.

ANS Please reference Figure 8.22