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General References

More detailed descriptions of the chemistry of the main group elements can be found in N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements,* 2nd ed., Butterworth-Heinemann, London, 1997, and in F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman, *Advanced Inorganic Chemistry,* 6th ed., Wiley InterScience, New York, 1999. A handy reference on the properties of the elements themselves, including many physical properties, is J. Emsley, *The Elements*, 3rd ed., Oxford University Press, 1998. For extensive structural information on inorganic compounds, see A. F. Wells, *Structural Inorganic Chemistry,* 5th ed., Clarendon Press, Oxford, 1984. Three useful references on the chemistry of nonmetals are R. B. King, *Inorganic Chemistry of Main Group Element*, VCH Publishers, New York, 1995; P. Powell and P. Timms, *The Chemistry of the Nonmetals*, Chapman and Hall, London, 1974; and R. Steudel, *Chemistry of the Non-Metals*, Walter de Gruyter, Berlin, 1976, English edition by F. C. Nachod and J. J. Zuckerman. The most complete reference on chemistry of the main group compounds through the early 1970s is the five-volume set by J. C. Bailar, Jr., H. C. Emeléus, R. Nyholm, and A. F. Trotman-Dickinson, editors, *Comprehensive Inorganic Chemistry*, Pergamon Press, Oxford, 1973. Two recent references on fullerene and related chemistry are A. Hirsch and M. Brettreich, *Fullerenes*, Wiley-VCH, Weinheim, Germany, 2005, and F. Langa and J.-F. Nierengarten, editors, *Fullerenes, Principles, and Applications*, RSC Publishing, Cambridge, UK, 2007. For entertaining and informative commentary and numerous photographs of all the elements that lend themselves to photos, see T. Gray, *The Elements*, Black Dog & Leventhal, New York, 2009.

Problems

8.1 The ions H_2^+ and H_3^+ have been observed in gas discharges.
   a. H_2^+ has been reported to have a bond distance of 106 pm and a bond dissociation enthalpy of 255 kJ mol^{-1}. Comparable values for the neutral molecule are 74.2 pm and 436 kJ mol^{-1}. Are these values for H_2^+ in agreement with the molecular orbital picture of this ion? Explain.
   b. Assuming H_3^+ to be triangular (the probable geometry), describe the molecular orbitals of this ion and determine the expected H—H bond order.

8.2 The species He_2^+ and HeH^+ have been observed spectroscopically. Prepare molecular orbital diagrams for these two ions. What would you predict for the bond order of each?

8.3 The chemical species IF_4^- and XeF_4 are known. Is the isoelectronic ion CsF_4^+ plausible? If it could be made, predict and sketch its most likely shape. Comment on whether such an ion might or might not be possible.

8.4 The equilibrium constant for the formation of the cryptand $\left[Sr\left\{ cryptand(2.2.1) \right\} \right]^{2+}$ is larger than the equilibrium constants for the analogous calcium and barium cryptands. Suggest an explanation. (See E. Kauffmann, J-M. Lehn, J-P. Sauvage, *Helv. Chim. Acta*, **1976**, *59*, 1099.)

8.5 Gas phase BeF_2 is monomeric and linear. Prepare a molecular orbital description of the bonding in BeF_2.

8.6 In the gas phase, $BeCl_2$ forms a dimer of the following structure:

$$Cl-Be\underset{Cl}{\overset{Cl}{\diagup\diagdown}}Be-Cl$$
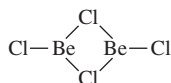
   Describe the bonding of the chlorine bridges in this dimer in molecular orbital terms.

8.7 BF can be obtained by reaction of BF_3 with boron at 1850 °C and low pressure; BF is highly reactive but can be preserved at liquid nitrogen temperature (77 K). Prepare a molecular orbital diagram of BF. How would the molecular orbitals of BF differ from CO, with which BF is isoelectronic?

8.8 N-heterocyclic carbenes, such as the example shown here, have become increasingly important in both main group and transition-metal chemistry. For example, the first report of a stable neutral molecule having a boron–boron double bond used this N-heterocyclic carbene to bond to each of the borons in a product of the reaction of **R**BBr$_3$ with the powerful reducing agent KC$_8$ (potassium graphite) in diethylether solvent. (See Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.*, **2007**, *129*, 12412.)
   a. What was the structure of this first molecule with a B $=$ B bond? What evidence was cited for a double bond?
   b. If **R**SiCl$_4$ was used in place of **R**BBr$_3$, an equally notable silicon compound was formed. What was this compound, and what parallels were noted with the reaction in Part **a**? (See Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science*, **2008**, *321*, 1069.)
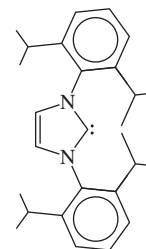

R, an N-heterocyclic carbene

8.9 $Al_2(CH_3)_6$ is isostructural with diborane, B_2H_6. On the basis of the orbitals involved, describe the Al—C—Al bonding for the bridging methyl groups in $Al_2(CH_3)_6$.

8.10 Referring to the description of bonding in diborane in Figure 8.12:

    a. Show that the representation $\Gamma(p_z)$ reduces to $A_g + B_{1u}$.

    b. Show that the representation $\Gamma(p_x)$ reduces to $B_{2g} + B_{3u}$.

    c. Show that the representation $\Gamma(1s)$ reduces to $A_g + B_{3u}$.

    d. Using the D_{2h} character table, verify that the sketches for the group orbitals match their respective symmetry designations (A_g, B_{2g}, B_{1u}, B_{3u}).

8.11 The compound $C(PPh_3)_2$ is bent at carbon; the P—C—P angle in one form of this compound has been reported as 130.1°. Account for the nonlinearity at carbon.

8.12 The C—C distances in carbides of formula MC_2 are in the range 119 to 124 pm if M is a Group 2 (IIA) metal or other metal commonly forming a 2+ ion, but in the approximate range 128 to 130 pm for Group 3 (IIIB) metals, including the lanthanides. Why is the C—C distance greater for the carbides of the Group 3 metals?

8.13 The half-life of ^{14}C is 5730 years. A sample taken for radiocarbon dating was found to contain 56 percent of its original ^{14}C. What was the age of the sample? (Radioactive decay of ^{14}C follows first-order kinetics.)

8.14 Prepare a model of buckminsterfullerene, C_{60}. By referring to the character table, verify that this molecule has I_h symmetry.

8.15 Determine the point groups of the following:

    a. The unit cell of diamond

    b. C_{20}

    c. C_{70}

    d. The nanoribbons shown in Figure 8.18

8.16 What is graph*ane*? How has it been synthesized, and what might be some of its potential uses? (See D. C. Elias, et al., *Science*, **2009**, *323*, 610.)

8.17 Prepare a sheet showing an extended graphene structure, approximately 12 by 15 fused carbon rings or larger. Use this sheet to show how the graphene structure could be rolled up to form (**a**) a zigzag nanotube, (**b**) an armchair nanotube, and (**c**) a chiral nanotube. Is more than one chiral structure possible? (See M. S. Dresselhaus, G. Dresselhaus, and R. Saito, *Carbon*, **1995**, *33*, 883.)

8.18 To what extent has using carbon nanotubes for delivery of the anticancer agent cisplatin shown promise in the killing of cancer cells? (See J. F. Rusling, J. S. Gutkind, A. A. Bhirde, et al., *ACS Nano*, **2009**, *3*, 307.) The reader is encouraged to search the recent literature to find more up to date references in this ongoing area of research.

8.19 What accounts for the relationship between the color of armchair carbon nanotubes and their diameter? See E. H. Hároz, J. G. Duque, B. Y. Lu, P. Nikolaev, S. Arepalli, R. H. Hauge, S. K. Doorn, J. Kono, *J. Am. Chem. Soc.*, **2012**, *134*, 4461.

8.20 Explain the increasing stability of the 2+ oxidation state for the Group 14 (IVA) elements with increasing atomic number.

8.21 1,2-Diiododisilane has been observed in both *anti* and *gauche* conformations. (See K. Hassler, W. Koell, K. Schenzel, *J. Mol. Struct.*, **1995**, *348*, 353.) For the *anti* conformation, shown here,
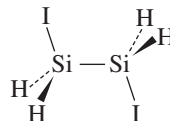
    a. What is the point group?

    b. Predict the number of infrared-active silicon–hydrogen stretching vibrations.

8.22 The reaction $P_4(g) \rightleftharpoons 2\ P_2(g)$ has $\Delta H = 217\ kJ\ mol^{-1}$. If the bond energy of a single phosphorus–phosphorus bond is 200 kJ mol^{-1}, calculate the bond energy of the P≡P bond. Compare the value you obtain with the bond energy in $N_2(946\ kJ\ mol^{-1})$, and suggest an explanation for the difference in bond energies in P_2 and N_2.

8.23 The azide ion, N_3^-, is linear with equal N—N bond distances.

    a. Describe the pi molecular orbitals of azide.

    b. Describe in HOMO-LUMO terms the reaction between azide and H^+ to form hydrazoic acid, HN_3.

    c. The N—N bond distances in HN_3 are given in Figure 8.30. Explain why the terminal N—N distance is shorter than the central N—N distance in this molecule.

8.24 In aqueous solution, hydrazine is a weaker base than ammonia. Why? (pK_b values at 25 °C: NH_3, 4.74; N_2H_4, 6.07)

8.25 The bond angles for the hydrides of the Group 15 (VA) elements are as follows: NH_3, 107.8°; PH_3, 93.6°; AsH_3, 91.8°; and SbH_3, 91.3°. Account for this trend.

8.26 Gas-phase measurements show that the nitric acid molecule is planar. Account for the planarity of this molecule.

8.27 With the exception of NO_4^{3-}, all the molecules and ions in Table 8.10 are planar. Assign their point groups.

8.28 The uncatalyzed isomerization for *cis*-N_2F_2 and *trans*-N_2F_2 has been examined via computational techniques (K. O. Christe, D. A. Dixon, D. J. Grant, R. Haiges, F. S. Tham, A. Vij, V. Vij, T.-H. Wang, W. W. Wilson, *Inorg. Chem.*, **2010**, *49*, 6823).

    a. Which isomer has the lower electronic ground state at 298 K (and by how much) on the basis of the computational work?

    b. Describe the proposed isomerization mechanisms. Which has a lower activation barrier (and by how much)?

    c. Using SbF_5 as the Lewis acid, draw a Lewis structure of the species proposed to lower the isomerization barrier for *trans*-N_2F_2. Which mechanism is presumed to be operative in this case? Describe the expected geometric changes in the *trans*-N_2F_2/SbF_5 adduct, and how these facilitate the isomerization.

8.29 Use the Latimer diagrams for phosphorus in Appendix B.7 to construct Frost diagrams for acidic and basic conditions. Provide balanced reduction half-reactions for all adjacent couples in these Latimer diagrams.

8.30 What type of interaction holds the O_2 units together in the O_8 structure? How does this interaction stabilize the larger molecule? (Hint: consider the molecular orbitals of O_2. See R. Steudel, M. W. Wong, *Angew. Chem., Int. Ed.*, **2007**, *46*, 1768.)

8.31 The sulfur–sulfur distance in S_2, the major component of sulfur vapor above ~720° C, is 189 pm, significantly shorter than the sulfur–sulfur distance of 206 pm in S_8. Suggest an explanation for the shorter distance in S_2. (See C. L. Liao, C. Y. Ng, *J. Chem. Phys.*, **1986**, *84*, 778.)

8.32 Because of its high reactivity with most chemical reagents, F_2 is ordinarily synthesized electrochemically. However, the chemical synthesis of F_2 has been recorded via the reaction

$$2 \ K_2MnF_6 + 4 \ SbF_5 \longrightarrow 4 \ KSbF_6 + 2 \ MnF_3 + F_2$$
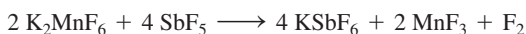
This reaction can be viewed as a Lewis acid–base reaction. Explain. (See K. O. Christe, *Inorg. Chem.*, **1986**, *25*, 3722.)

8.33 a. Chlorine forms a variety of oxides, among them Cl_2O and Cl_2O_7. Cl_2O has a central oxygen; Cl_2O_7 also has a central oxygen atom, bridging two ClO_3 groups. Of these two compounds, which would you predict to have the smaller $Cl-O-Cl$ angle? Explain briefly.

   b. The dichromate ion, $Cr_2O_7^{2-}$, has the same structure as Cl_2O_7, with oxygen now bridging two CrO_3 groups. Which of these two oxygen-bridged species do you expect to have the smaller outer atom–O–outer atom angle? Explain briefly.

8.34 The triiodide ion I_3^- is linear, but I_3^+ is bent. Explain.

8.35 Although B_2H_6 has D_{2h} symmetry, I_2Cl_6 is planar. Account for the difference in the structures of these two molecules.

8.36 BrF_3 undergoes autodissociation according to the equilibrium

$$2 \ BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Ionic fluorides such as KF behave as bases in BrF_3, whereas some covalent fluorides such as SbF_5 behave as acids. On the basis of the solvent system concept, write balanced chemical equations for these acid–base reactions of fluorides with BrF_3.

8.37 The diatomic cations Br_2^+ and I_2^+ are both known.

   a. On the basis of the molecular orbital model, what would you predict for the bond orders of these ions? Would you predict these cations to have longer or shorter bonds than the corresponding neutral diatomic molecules?

   b. Br_2^+ is red, and I_2^+ is bright blue. What electronic transition is most likely responsible for absorption in these ions? Which ion has the more closely spaced HOMO and LUMO?

   c. I_2 is violet, and I_2^+ is blue. On the basis of frontier orbitals (identify them), account for the difference in their colors.

8.38 I_2^+ exists in equilibrium with its dimer I_4^{2+} in solution. I_2^+ is paramagnetic and the dimer is diamagnetic. Crystal structures of compounds containing I_4^{2+} have shown this ion to be planar and rectangular, with two short $I-I$ distances (258 pm) and two longer distances (326 pm).

   a. Using molecular orbitals, propose an explanation for the interaction between two I_2^+ units to form I_4^{2+}.

   b. Which form is favored at high temperature, I_2^+ or I_4^{2+}? Why?

8.39 How many possible isomers are there of the ion $IO_2F_3^{2-}$? Sketch these, and indicate the point group for each. The observed ion has IR-active iodine–oxygen stretches at 802 and 834 cm^{-1}. What does this indicate about the most likely structure? (See J. P. Mack, J. A. Boatz, M. Gerken, *Inorg. Chem.*, **2008**, *47*, 3243.

8.40 What is a **superhalogen**? Does it contain a halogen? By searching the literature, find the earliest reference to this term and the rationale for the name "superhalogen." Also provide examples of modern chemical applications of superhalogens.

8.41 Bartlett's original reaction of xenon with PtF_6 apparently yielded products other than the expected $Xe^+PtF_6^-$. However, when xenon and PtF_6 are reacted in the presence of a large excess of sulfur hexafluoride, $Xe^+PtF_6^-$ is apparently formed. Suggest the function of SF_6 in this reaction. (See: K. Seppelt, D. Lentz, *Progr. Inorg. Chem.*, **1982**, *29*, 170.)

8.42 On the basis of VSEPR, predict the structures of $XeOF_2$, $XeOF_4$, XeO_2F_2, and XeO_3F_2. Assign the point group of each.

8.43 The sigma bonding in the linear molecule XeF_2 may be described as a three-center, four-electron bond. If the z axis is assigned as the internuclear axis, use the p_z orbitals on each of the atoms to prepare a molecular orbital description of the sigma bonding in XeF_2.

8.44 The $OTeF_5$ group can stabilize compounds of xenon in formal oxidation states IV and VI. On the basis of VSEPR, predict the structures of $Xe(OTeF_5)_4$ and $O=Xe(OTeF_5)_4$.

8.45 Write a balanced equation for the oxidation of Mn^{2+} to MnO_4^- by the perxenate ion in acidic solution; assume that neutral Xe is formed.

8.46 The ion XeF_5^- is a rare example of pentagonal planar geometry. On the basis of the symmetry of this ion, predict the number of IR-active Xe–F stretching bands.

8.47 $XeOF_4$ has one of the more interesting structures among noble gas compounds. On the basis of its symmetry,

   a. Obtain a representation based on *all* the motions of the atoms in $XeOF_4$.

   b. Reduce this representation to its component irreducible representations.

   c. Classify these representations, indicating which are for translational, rotational, and vibrational motion.

8.48 The ion XeF_2^{2-} has not been reported. Would you expect this ion to be bent or linear? Suggest why it remains elusive.

8.49 Photolysis of a solid mixture of H_2O, N_2O, and Xe at 9 K, followed by annealing, gave a product identified as HXeOXeH (L. Khriachtchev, K. Isokoski, A. Cohen, M. Räsänen, R. B. Gerber, *J. Am. Chem. Soc.*, **2008**, *130*, 6114). Supporting evidence included infrared data, with a band at 1379.7 cm^{-1}, assigned to Xe—H stretching. When the experiment was repeated using deuterated water

containing both D_2O and H_2O, bands at 1432.7 cm^{-1}, 1034.7 cm^{-1}, and 1003.3 cm^{-1}, were observed, together with the band at 1379.7 cm^{-1}. Account for the infrared data from the experiment conducted using deuterated water.

8.50 Use the Latimer diagram for xenon in basic solution in Appendix B.7 to:
   a. Construct balanced half-reactions for the $HXeO_6^{3-}/HXeO_4^-$ and $HXeO_4^-/Xe$ redox couples.
   b. Use these half-reactions to show that the disproportionation of $HXeO_4^-$ in basic solution is spontaneous by calculating E^o and ΔG^o for the reaction.

8.51 Although atmospheric ozone depletion is a widely known phenomenon, the estimate that as much as 90% of the xenon originally in Earth's atmosphere is now absent is largely unknown. The synthesis and study of XeO_2 (D. S. Brock, G. J. Schrobilgen, *J. Am. Chem. Soc.*, **2011**, *133*, 6265) supports the hypothesis that the reaction of SiO_2 from the Earth's core with Xe may be responsible for the depletion of this noble gas.
   **a.** Describe how the synthesis of XeO_2 is carried out, including the reactants, conditions, temperature sensitivity, and hazards associated with the synthesis.
   b. Explain why monomeric XeO_2 would likely be soluble in water.
   c. Raman spectroscopic studies were vital to characterize XeO_2. What experimental observation suggested that XeO_2 only contains Xe—O bonding? What experimental observation suggested that XeO_2 did not contain any hydrogen atoms?

8.52 Liquid NSF_3 reacts with $[XeF][AsF_6]$ to form $[F_3SNXeF][AsF_6]$, **1**. On mild warming in the solid state, compound **1** rearranges to $[F_4SNXe][AsF_6]$, **2**. Reaction of compound **2** with HF yields $[F_4SNH_2][AsF_6]$, **3**, $[F_5SN(H)Xe][AsF_6]$, **4**, and XeF_2. (See G. L. Smith, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.*, **2007**, *46*, 1369; *Inorg. Chem.*, **2008**, *47*, 4173; and *J. Am. Chem. Soc.*, **2009**, *131*, 4173.)
   a. What is the bond order in $[XeF]^+$?
   b. Of compounds **1** through **4**, which has the longest S—N distance? The shortest?
   c. Which of the compounds **1** through **4** is most likely to have linear bonding around the nitrogen atom?
   d. By the VSEPR approach, is the bonding around Xe expected to be linear or bent in compound **1**?
   e. In compounds **2** and **3**, are the NXe and NH_2 groups likely to occupy axial or equatorial sites on sulfur?
   f. In compounds **2** and **3**, which bonds are more likely to be longer, the $S—F_{axial}$ bonds or $S—F_{equatorial}$ bonds?

8.53 Determine the point groups:
   a. O_8 (Figure 8.34)
   b. S_8 (Figure 8.35)
   c. A chiral nanotube
   d. The section of β-graphyne shown in Figure 8.23
   e. $Xe_3OF_3^+$
   f. The proposed very high pressure form of oxygen, spiral-chain O_4 (L. Zhu, Z. Wang, Y. Wang, G. Zou, H. Mao, Y. Ma, *Proc. Nat. Acad. Sci.*, **2012**, *109*, 751).
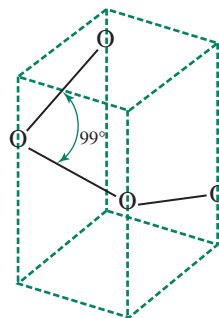
The following problems require the use of molecular modeling software.

8.54 It has been proposed that salts containing the cation $[FBeNg]^+$, where $Ng = $ He, Ne, or Ar, may be stable. Use molecular modeling software to calculate and display the molecular orbitals of $[FBeNe]^+$. Which molecular orbitals would be the primary ones engaged in bonding in this ion? (See M. Aschi, F. Grandinetti, *Angew. Chem., Int. Ed.*, **2000**, *39*, 1690.)

8.55 The dixenon cation Xe_2^+ has been characterized structurally. Using molecular modeling software, calculate and observe the energies and shapes of the molecular orbitals of this ion. Classify each of the seven highest-energy occupied orbitals as σ, π, or δ, and as bonding or antibonding. The bond in this compound was reported as the longest main group–main group bond observed to date. Account for this very long bond. (See T. Drews, K. Seppelt, *Angew. Chem., Int. Ed.*, **1997**, *36*, 273.)

8.56 To further investigate the bonding in the O_8 structure, construct an O_8 unit, and calculate and display its molecular orbitals. Which orbitals are involved in holding the O_2 units together? In each of these orbitals, identify the atomic orbitals that are primarily involved. (See Figure 8.34; additional structural details can be found in L. F. Lundegaard, G. Weck, M. I. McMahon, S. I. Desgreniers, P. Loubeyre, *Science*, **2006**, *443*, 201 and R. Steudel, M. W. Wong, *Angew. Chem., Int. Ed.*, **2007**, *46*, 1768.)