Chem 370 - Spring, 2019 Assignment 10 - Solutions

- 8.20 The stability of the bonds decreases rapidly down the group, but the ionization energy declines less rapidly. In the case of lead, the ionization energy to the +4 state is actually greater than that of tin. Therefore, the +2 state becomes increasingly favorable, because it requires less energy input for ionization. The tendency is sometimes called the "inert pair effect."
- 8.22 To bring about the change $P_4(g) \approx 2 P_2(g)$, the six bonds of the P_4 tetrahedron must be broken and two new $P \equiv P$ triple bonds must be made. The sum of the endothermic bond breaking and exothermic bond forming is the enthalpy of the reaction.

 $\Delta H = 6 D_{\text{P-P}} - 2 D_{\text{P=P}} = 217 \text{ kJ} = (6)(200 \text{ kJ}) - 2 D_{\text{P=P}}$ $D_{\text{P=P}} = \{(6)(200 \text{ kJ}) - 217 \text{ kJ}\}/2 = 491.5 \text{ kJ} = 492 \text{ kJ}$

Compared to the triple bond in N₂ (D = 946 kJ), this is a much weaker bond. The 3p orbitals on the much bigger P atoms do not overlap as effectively as the 2p orbitals on N, so the $p\pi$ bonding in P=P is much weaker.

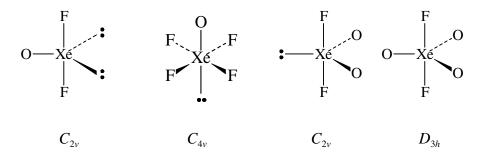
- 8.25 As the central atom becomes larger, the lone pair's influence on the geometry declines. The three hydrogen atoms maintain a relatively similar nonbonding separation in all cases, which is achieved with a smaller bond angle as the central atom becomes larger. The trend is consistent with Ligand Close Packing (LCP) considerations.
- 8.31 Gaseous S₂ has a similar MO scheme to that of O₂, being paramagnetic and having a bond order of two. The MO scheme responsible for the bonding is $(\sigma_{3p})^2 (\pi_{3p})^4 (\pi^*_{3p})^2$. In S₈ the S–S bonds have a bond order of one and therefore are longer.
- 8.34 The bent structure is predicted by VSEPR considerations.

8.36 By the solvent system concept, the cation BrF_2^+ defines the acid species and the anion BrF_4^- defines the base species in $BrF_3(l)$.

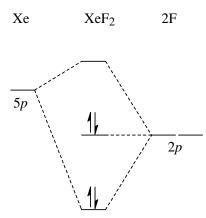
$F^- + BrF_3 \rightleftharpoons BrF_4^-$	basic solution
$SbF_5 + BrF_3 \rightleftharpoons SbF_6^- + BrF_2^+$	acidic solution

8.42 In all of these the oxygen atom occupies a position that allows it more room, such as an equatorial position of a trigonal bipyramid. The Xe–O bond is often represented as a double bond (Xe=O), although this is not necessary (or even helpful) in deducing the structures.

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8.43 The fluorine SALCS are Σ_{g}^{+} and Σ_{u}^{+} in $D_{\omega h}$, and are the combinations $\psi_{1} + \psi_{2}$ and $\psi_{1} - \psi_{2}$, respectively. The $5p_{z}$ orbital on Xe transforms as Σ_{u}^{+} and therefore can form bonding and antibonding combinations with the same-symmetry SALC. The Σ_{g}^{+} SALC in this model is taken to be nonbonding, although it could form bonding and antibonding combinations with the 5*s* orbital on Xe. The MO scheme is shown below.



As shown, this MO scheme has only one pair in a bonding MO, which would suggest that the F–Xe–F linkage is a 3c-2e bond. However, if the Σ_g^+ SALC interacts with Xe 5s, then the level shown as nonbonding in the scheme above would become bonding, making the linkage a 3c-4e bond.

8.45 Perxenate is a powerful oxidant, capable of oxidizing Mn^{2+} to MnO_4^{-} .

 $\begin{array}{rcl} 8(Mn^{2+} + 4H_2O & \rightarrow & MnO_4^- + 8H^+ + 5e^-) \\ 5(XeO_6^{4-} + 12H^+ + 8e^- & \rightarrow & Xe + 6H_2O) \\ \end{array}$ $8Mn^{2+} + 5XeO_6^{4-} + 2H_2O & \rightarrow 8MnO_4^- + 4H^+ + 5Xe \\ \end{array}$

- 2. Balanced equations:
- a. $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$
- b. $3CH_2(CO_2H)_2 + P_4O_{10} \rightarrow 2C_3O_2 + 4H_3PO_4$
- c. $PbS + O_2 \xrightarrow{\Delta} Pb + SO_2$
- d. $Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3$
- e. $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$
- f. $GeCl_4 + Ge \rightarrow 2GeCl_2$
- g. $2Ca_3(PO_4)_2 \cdot 2H_2O + 6SiO_2 + 10C$ $\overrightarrow{\Delta}$ $6CaSiO_3 + P_4 + 10CO + 4H_2O$
- h. $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ (at moderate temperature) $NH_4NO_3 \xrightarrow{\Delta} N_2 + \frac{1}{2}O_2 + 2H_2O$ (at high temperature - explosion!)
- i. $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$
- j. $PH_3 + 2I_2 + 2H_2O \rightarrow H_3PO_2 + 4HI$
- k. $BaO_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2$
- 1. $SO_3 + H_2O \rightarrow H_2SO_4$
- m. $SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$
- n. $CaF_2 + H_2SO_4 \xrightarrow{\Delta} 2HF(g) + CaSO_4(s)$
- o. $Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O$
- p. $6NH_4ClO_4 + 8Al \rightarrow 4Al_2O_3 + 3N_2 + 3Cl_2 + 12H_2O_3$
- q. Xe + $F_2 \xrightarrow{hv} XeF_2$
- r. $4XeF_4 + 8H_2O \rightarrow 2Xe + O_2 + 16HF + 2XeO_3$ (violent!)

s.
$$2C_6H_6 + XeF_2 \rightarrow 2C_6H_5F + Xe + H_2$$

- 3. Name reactions and processes:
- a. Preparation of pure silicon

 $\begin{array}{ll} \text{SiCl}_4 + 2\text{H}_2 & \xrightarrow{\text{hot Ta wire}} & \text{Si} + 4\text{HCl} & \text{OR} \\ \text{SiI}_4 & \xrightarrow{\text{hot Ta wire}} & \text{Si} + 2\text{I}_2 & & \text{followed by zone refining} \end{array}$

b. Haber process

$$3H_2 + N_2 = \frac{500 \text{ oC}/250 \text{ atm/Fe}}{2NH_3}$$

- c. Raschig synthesis $2NH_3 + OCl^- \xrightarrow{glue} N_2H_4 + Cl^- + H_2O$
- d. Ostwald process

 $4NH_3 + 5O_2 \xrightarrow{750-850 \text{ oC}} 4NO + 6H_2O$ $2NO + O_2 \rightarrow 2NO_2$ $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

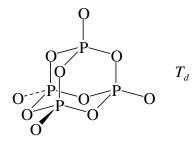
- e. Contact process for making sulfuric acid $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$ $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$ $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
- f. Synthesis of fluorine $2KHF_2 \xrightarrow{\text{electrolysis}} H_2 + F_2 + 2KF$
- g. Industrial synthesis of hydrochloric acid

$$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$

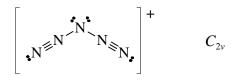
- 4. Structures
- a. Carbon suboxide

$$\overset{\bullet}{O} = C = C = \overset{\bullet}{O} \quad D_{\sim h}$$

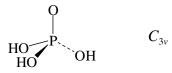
b. P₄O₁₀



c. N_5^+ ion



d. Orthophosphoric acid



e. Xenon trioxide

