

**Chem 370 - Spring, 2019**  
**Assignment 10 - Solutions**

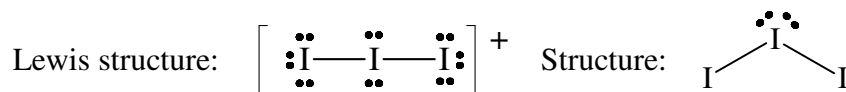
- 8.20 The stability of the bonds decreases rapidly down the group, but the ionization energy declines less rapidly. In the case of lead, the ionization energy to the +4 state is actually greater than that of tin. Therefore, the +2 state becomes increasingly favorable, because it requires less energy input for ionization. The tendency is sometimes called the "inert pair effect."
- 8.22 To bring about the change  $P_4(g) \rightleftharpoons 2 P_2(g)$ , 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.

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

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

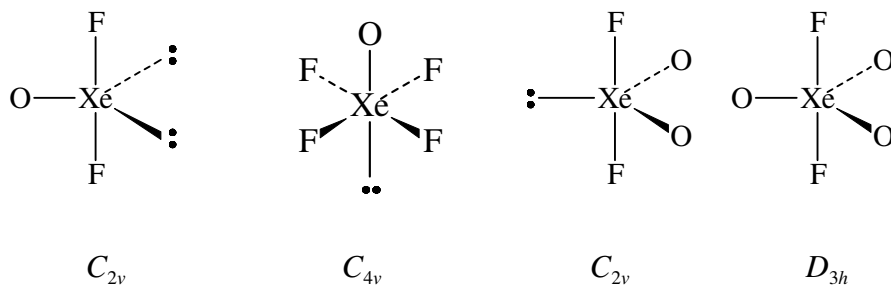
Compared to the triple bond in  $N_2$  ( $D = 946 \text{ kJ}$ ), this is a much weaker bond. The  $3p$  orbitals on the much bigger P atoms do not overlap as effectively as the  $2p$  orbitals on N, so the  $p\pi$  bonding in  $P \equiv P$  is much weaker.

- 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  $S_2$  has a similar MO scheme to that of  $O_2$ , 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  $S_8$  the S-S bonds have a bond order of one and therefore are longer.
- 8.34 The bent structure is predicted by VSEPR considerations.

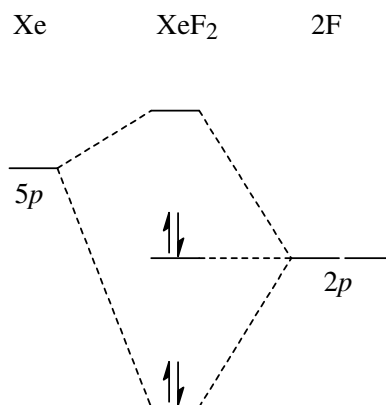


- 8.36 By the solvent system concept, the cation  $BrF_2^+$  defines the acid species and the anion  $BrF_4^-$  defines the base species in  $BrF_3(l)$ .
- $$F^- + BrF_3 \rightleftharpoons BrF_4^- \quad \text{basic solution}$$
- $$SbF_5 + BrF_3 \rightleftharpoons SbF_6^- + BrF_2^+ \quad \text{acidic solution}$$

- 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.

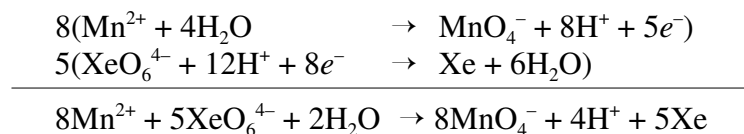


- 8.43 The fluorine SALCS are  $\Sigma_g^+$  and  $\Sigma_u^+$  in  $D_{\infty h}$ , and are the combinations  $\psi_1 + \psi_2$  and  $\psi_1 - \psi_2$ , respectively. The  $5p_z$  orbital on Xe transforms as  $\Sigma_u^+$  and therefore can form bonding and antibonding combinations with the same-symmetry SALC. The  $\Sigma_g^+$  SALC in this model is taken to be nonbonding, although it could form bonding and antibonding combinations with the  $5s$  orbital on Xe. The MO scheme is shown below.

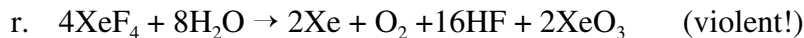
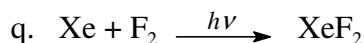
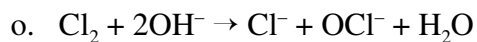
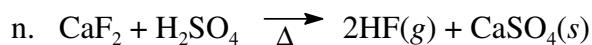
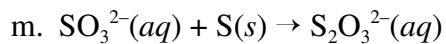
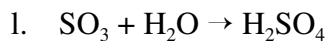
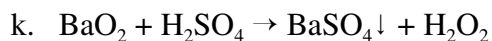
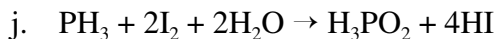
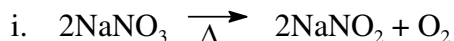
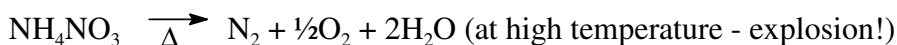
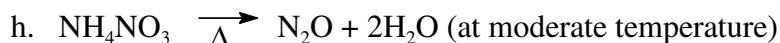
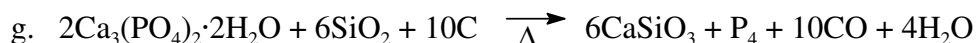
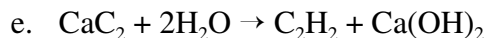
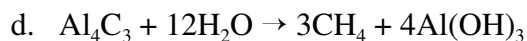
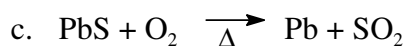
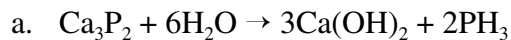


As shown, this MO scheme has only one pair in a bonding MO, which would suggest that the F–Xe–F linkage is a  $3c-2e$  bond. However, if the  $\Sigma_g^+$  SALC interacts with Xe  $5s$ , then the level shown as nonbonding in the scheme above would become bonding, making the linkage a  $3c-4e$  bond.

- 8.45 Perxenate is a powerful oxidant, capable of oxidizing  $\text{Mn}^{2+}$  to  $\text{MnO}_4^-$ .

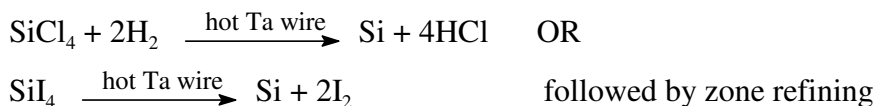


2. Balanced equations:

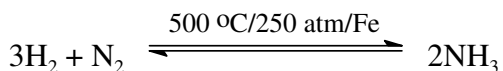


3. Name reactions and processes:

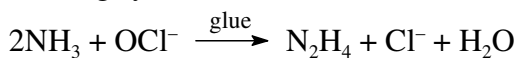
a. Preparation of pure silicon



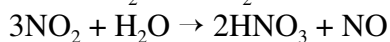
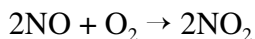
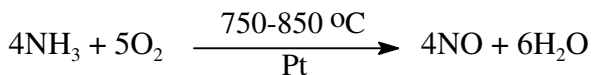
b. Haber process



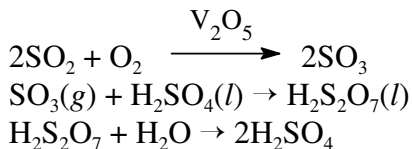
c. Raschig synthesis



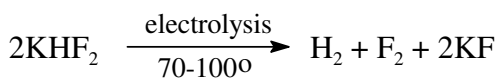
d. Ostwald process



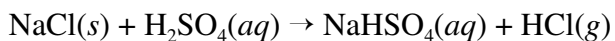
e. Contact process for making sulfuric acid



f. Synthesis of fluorine

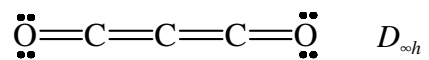
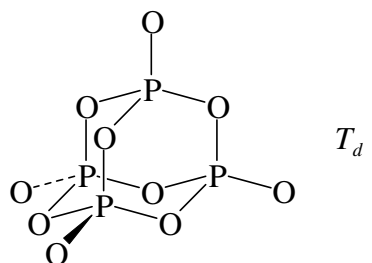
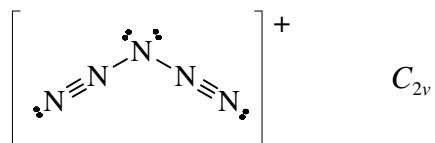


g. Industrial synthesis of hydrochloric acid

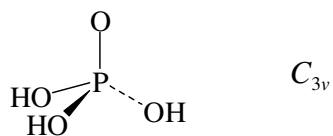


## 4. Structures

## a. Carbon suboxide

b.  $\text{P}_4\text{O}_{10}$ c.  $\text{N}_5^+$  ion

## d. Orthophosphoric acid



## e. Xenon trioxide

