HW 10
CHEM 362

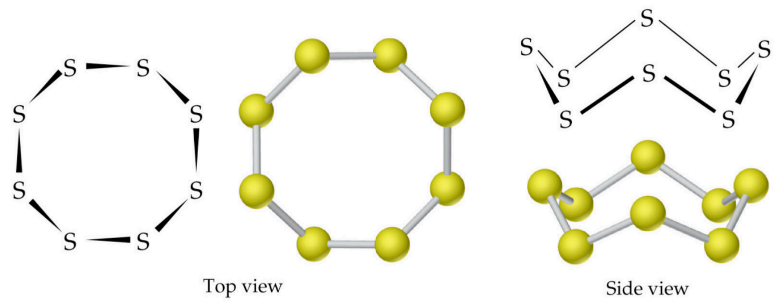
Due: November 26, 2019

1. Why do all noble gases have very high first ionization energies?

   Noble gases have an electron configuration in which the orbitals are completely full. As such, they are already very stable and it would be difficult to remove an electron

2. Draw the structure of the most stable form of sulfur

   S_8



3. a) Why are bonds between second row elements shorter than third row elements?

   Third row atoms are larger, and valence orbitals are larger too.

   b) Why are Si=Si bonds unfavorable, compared to C=C bonds?

   pi-pi overlap (to make the double bond) is not as optimal for Si as it is for C. This can be attributed to the size of the silicon atoms compared to the carbon atoms, as well as increased repulsion between silicon atoms due to fully filled 2p orbitals

4. What is the octet rule? Why does it apply strictly only to elements of the first short period?

   Octet rule: an element in a covalent substance typically acquires eight electrons, either lone or bonded. Elements in rows three and below can accommodate electrons in orbitals other than s and p, and so exceptions to the octet rule may be observed.

5. 4d and 5d metals have a smaller atomic radius than one might expect.

a) What phenomenon is responsible for this? Describe

Lanthanide contraction: the trend in the 4f elements to shrink a great deal to a huge increase in the effective nuclear charge as one adds subsequent electrons to the same shell. This occurs because f orbitals are not very good at shielding the s and d orbitals above them. The shielding effect exerted by the inner electrons decreases in order s > p > d > f. Usually, as a particular subshell is filled in a period, atomic radii decreases. This effect is particularly pronounced in the case of lanthanides, as their 4f subshells are being filled across the period and they are less and less able to shield the outer (5th and 6th) shell electrons. Thus the shielding effect is less able to counter the decrease in radius caused by increasing nuclear charge.The result is that the second and third rows of the d-block transition metals have nearly the same atomic sizes.

b) Of the pairs of elements given, indicate which would have the larger atomic radii

i) Eu vs **Pr**
ii) **Sm** vs Tm
iii) **Ce** vs Dy

6. What are the six properties of transition metals?

(1) All are metals
(2) Practically all are hard, high melting, high boiling elements that are good conductors
(3) They form alloys with each other
(4) Many are highly electropositive such that they dissolve in mineral acids (oxidized)
(5) They exhibit variable valence
(6) They form paramagnetic compounds

7. For each of the following, classify as hard or soft acid or base, and explain why you chose that classification

Hard Acids: High positive charge, small size, not easily polarizable. **Hard Bases:** Low polarizability, high electronegativity, not easily oxidized. **Soft Acids:** Low positive charge, large size, easily oxidized, highly polarizable. **Soft Base:** High polarizability, diffuse donor orbital, low electronegativity, easily oxidized

i) Fe^{3+} **HA**
ii) H^- **SB**
iii) CO_3^{2-} **HB**
iv) CO **SB**
v) Ag^+ **SA**
vi) HO^+ **SA**
vii) OH^- **HB**
viii) Li^+ **HA**

8. In terms of the HSAB concept, which end of the SCN^- ion would you expect to coordinate to Cr^{3+}? To Pt^{2+}?

Cr^{3+} is considered hard, therefore you should expect the N end to coordinate
Pt^{2+} is considered soft, therefore you should expect the S end to coordinate.

9. Would you expect the following reactions to proceed as written? Why or why not?

i) $AsF_3 + PI_3 \rightarrow AsI_3 + PF_3$
Yes: As^{3+} is softer than P^{3+} and I^- is softer than F^-

ii) $CaS + BaO \rightarrow CaO + BaS$
Yes: Ba^{2+} is softer than Ca^{2+}, and it it would favour the softer S^{2-} over O^{2-}

iii) $TiF_4 + 2TiI_2 \rightarrow TiI_4 + 2TiF_2$
No: Ti^{4+} is hard and F^- is hard, while I^- is softer.

iv) $Cu_2S + H_2O \rightarrow Cu_2O + H_2S$
No: Cu^+ is soft and S^{2-} is soft, while O^{2-} is hard. The reactant Cu_2S would be favoured to form

10. How is hydrogen prepared? Write a chemical reaction for this process.

Hydrogen is prepared by the electrolysis of water. (Electrolysis of brine or steam reforming of hydrocarbons are also acceptable answers)

$$2\,H_2O \xrightarrow[\text{electrolysis}]{H_2SO_4} 2\,H_2 + O_2$$

The half reactions are:

(reduction) cathode: $4\,H^+ + 4e^- \rightarrow 2\,H_2$
(oxidation) anode: $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^-$