1 Cognitive reasoning in the chemical sciences 5.13

Some of the following questions are similar to questions which have been asked before. Others are exactly the same as previous questions. And some are brand new types of questions. Please do all of these problems without referring to any prior work or class notes.

1. Please draw the nodes of the following orbitals.

   (a) $3p_{x+y}$

   (b) $5d_{x^2-z^2}$

2. An absolute maxiumum of ten adult clowns can fit into a Volkswagen Beetle. Clowns, like all humans, barely float in water. Estimate to within a factor of two how many liters of water a VW Beetle can hold.

3. The French scientist La Cheville-Tordue is studying real gases. She has determined the a and b parameters for carbon dioxide (CO_2), ammonia (NH_3), carbon disulfide (CS_2), dodecane ($C_{20}H_{42}$), and neon (Ne) for the van der Waals equation:

$$(p + a\frac{n^2}{V^2})(V - nb) = nRT.$$

   At 1 atm, ammonia and carbon dioxide are both gases, ammonia having the higher boiling point. At 1 atm, carbon disulfide and dodecane boil at respectively 46 and 216^{o}C

Compound	a (L^2atm/mol^2)	b (L/mol)
X	3.610	0.0427
Y	4.250	——
Z	11.10	0.0726
W	——	0.3758
Q	0.214	0.0171

   Unfortunately La Cheville Tordue has also forgotten to record two pieces of data in her table. Please, nonetheless, deduce which of the five compounds goes with which line of data.

4. For each of the following pairs of molecules, please draw the lowest energy way that you can envision for the two molecules to approach one another. Use dotted lines to indicate intermolecular attractions. To receive credit, you must show the correct shape of the actual molecules. **Please rank the energy of interaction 1 or 2 with 1 for the stronger intermolecular interaction and 2 for the weaker interaction** For credit please briefly explain your reasoning. What are the names of these intermolecular interactions?

   (a) BiH_3 and PoH_2

   (b) HCN and H_2O

5. Let's simplify a submarine to be just an iron hull surrounding a chamber of regular air. Let's assume this submarine floats under water, that is, it has the same average density as sea water. Iron has a density of 8 g/mL and to one significant figure seawater has the same density as fresh water/ For the submarine in this problem, what is the ratio of the volume of air to the volume of iron?

6. In a fluorine atmosphere an Fe-Co-C steel degrades into FeF_3(s), CoF_2(s) and CF_4(g). Exposed to hot selenium vapor this same steel degrades into FeSe(s), CoSe(s) and CSe_2(s). A 100.0 g sample of this steel in a fluorine atmosphere has a mass of 180.7 g after degradation, A similar 100.0 g sample exposed to a hot selenium vapor has a mass of 248.2 g. What was the original elemental composition of the steel?

7. The OH radical has been observed in interstellar space. In making an MO diagram for this molecule consider only the O $2p$ AOs and the H $1s$ AO. The O $2p$ AOs can combine with the H $1s$ orbital. Formulate the MO diagram noting that the O $2p$ AO energy is -15.8 eV and the H $1s$ AO energy is -13.6 eV. Correctly fill in your diagram with the correct number of electrons.

   The difference between the first ionization energies of OH and of a lone O atom are almost exactly the same. Explain the reason for this observation.

8. In B_2, it was not initially clear whether the π_{2p} orbital was higher or lower in energy than the σ_{2p} orbital. Draw the two possible MO diagrams, in both cases placing the correct number of electrons into the MO diagram. B_2 is experimentally observed to be paramagnetic. Does this observation resolve the debate as to which is the correct ordering of the MO levels? Calculate the bond order of B_2. Which of the following expressions is correct: B≡B, B=B, or B-B?

9. Please consider the diatomic molecule XeO. Note oxygen is more electronegative than xenon.

   (a) Please draw the Lewis structure (showing all non-zero formal charges) for the diatomic molecule XeO. Please use Roman numerals to indicate the oxidation states of the two atoms.

   (b) Draw the MO diagram for this same molecule. Assume there is $s-p$ hybridization.

   (c) Please state the bond order of the diatomic molecule XeO (a) based on the MO diagram and (b) the Lewis structure. Is XeO diamagnetic or paramagnetic?

   (d) How many different frequencies of light can be absorbed by the XeO molecule without an electron being emitted as a result of the received photon?

   (e) How many different frequencies of light can be absorbed without the molecule separating into two separate atoms as a result of the received light?

   (f) Is it possible for the XeO molecule to stay together if the bond order is zero. If it is possible explain how it is possible.

10. You are given the task of separating the following three chemicals which have been placed in the tube located nearest point **A** indicated in the picture below. No chemicals are initially at flasks located near points **B** or **C**. The entire system is sealed; no compounds can escape. The three chemicals are acetic acid (CH_3COOH), CH_3F, and Ge. Germanium has the same bonding structure as diamond. You are allowed to chill or heat the points **A**, **B**, and **C** to any fixed temperature you wish to. To what temperature will you place points **A**, **B**, and **C**. For credit, please briefly explain your reasoning.

    To solve this problem recall that light main group dispersion interactions are <1 kJ/mole, dipole-dipole interactions vary between <1 kJ/mol and 5 kJ/mol, oxygen hydrogen bonds are roughly 20 kJ/mol, fluorine hydrogen bonds are roughly 100-150 kJ/mole, and normal main-group covalent bonds are between 300-500 kJ/mol. Also recall room temperature corresponds to 2.5 kJ/mole.