1 Cognitive reasoning in the chemical science 5.2

1. *State whether the following pairs of statements are synonomous, ie., does knowing the facts in one set allow you to deduce the information in the other set and vice-a-versa. Please explain your answer.*

   (a) **An ideal gas**

   i. n are T constant. p increases by 40%.
   ii. n are T constant. V decreases by 40%.

   (b) **An electron in an atom/ion**

   i. The energy of the atom/ion's $3s$ orbital and the $3d$ orbital are to several significant figures exactly the same.
   ii. The atom/ion has only one electron.

   (c) **Main group diatomic molecule**

   i. A main group diatomic molecule has exactly six valence electrons. The molecule is paramagnetic.
   ii. A main group diatomic molecule has exactly six valence electrons. The π_x and π_y orbitals are lower in energy than both of the two σ_p orbitals.

   (d) **Mixing AOs on the same atom**

   i. A p_z atomic orbital is mixed with another AO, orbital X. The result of the mixing is another p orbital. The new mixed orbital is neither purely the p_z nor the X orbital.
   ii. The X orbital is a p orbital which is not the p_z, not the -p_z orbital, and not any coefficient times the p_z orbital.

   (e) **Effusion**

   i. T is constant. There are two gases, A and B, contained inside a flask where effusion can take place. The two gases are present in the flask in the same concentration. A effuses 30% faster than B.
   ii. T is constant. There are two gases, A and B, contained inside a flask where effusion can take place. The two gases are present in the flask in the same concentration. The mass of A is $\sqrt{1.3}$ greater than B.

   (f) **An electron in a box**

   i. n is doubled.
   ii. The number of places where the electron can be at its most probable position doubles.

   (g) **An electron in a box**

   i. n is doubled.
   ii. The number of places inside the box where the electron can be at its least probable position doubles.

2. **MO questions asked in previous 2070 courses**

(a) Draw one of two possible molecular orbital diagrams for SO (sulfur-oxygen), labelling the molecular orbitals as bonding, antibonding, σ, and π. Label the HOMO and the LUMO. Does the molecule have unpaired electron density?

(b) 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.

(c) 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.

(d) 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?

(e) Bond lengths vary as a function of bond order. Identify three different second row homonuclear diatomic molecules from the electron configurations given below. Which of the three molecules are paramagnetic? Show the three MO diagrams (with electron filling included) and rank the molecules in order of increasing bond length.

   i. $(\sigma_{2s})^2(\sigma_{2s}^*)^2$
   ii. $(\sigma_{2s})^2$
   iii. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p}^*)^4$