

General Chemistry C, Fall 2023

Problem Set 2

- Due date: 2023/10/4 10:00 AM.
 - Write down how you calculate the answer step-by-step (don't forget about the units).
 - Please upload a PDF file containing your answers to NTU COOL.
1. (3 pt) Explain why the third ionization energy of manganese is much higher than three times its first ionization energy ($IE_1 = 717.4 \text{ kJ/mol}$, $IE_2 = 1509 \text{ kJ/mol}$, $IE_3 = 3248 \text{ kJ/mol}$).

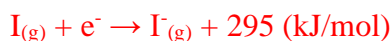
Electron configuration of Mn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5 = [\text{Ar}] 4s^2 3d^5$

As we know from the electron configuration of manganese, the first and second ionization energy is regarding ionizing the outer-shell electrons, which are 4s electrons. However, the third ionization energy is referred to as the first ejection of an inner-shell electron, which is a 3d electron. The consumption of energy due to the stronger interaction of electrostatics within the inner-shell electron than in the outer-shell electron results in the fact that the ionization of inner-shell electrons must consume more energy.

3pt for the comparison of “inner-shell electron 3d electron” and “outer-shell 4s electron” with reasonable explanation.

1pt for the electron configuration of Mn if the explanation is inappropriate.

2. (3 pt) The electron affinity of an iodine atom is 295 kJ/mol . Calculate the longest photon wavelength (in nm) required to eject an electron from an iodine anion in the gas phase.



$$E_{\text{photon}} = 295 \text{ (kJ/mol)} \times 1000 \text{ (J/kJ)} / 6.02 \times 10^{23} \text{ (1/mol)} = hc/\lambda$$

$$= 6.626 \times 10^{-34} \text{ (Js)} \times 3.00 \times 10^8 \text{ (m/s)} / \lambda \text{ (m)}$$

$$\lambda = 4.06 \times 10^{-7} \text{ (m)} = 406 \text{ (nm)}$$

The energy of photon should be “at least” equal to the ionization energy in the case of using light as an energy source to eject an electron. Hence, the longest photon wavelength required to eject an electron from an iodine anion in the gas phase would be 406 nm.

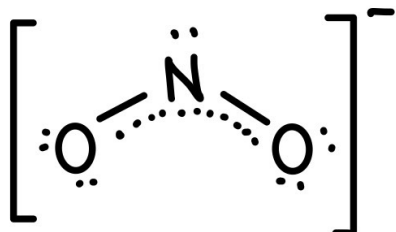
2 pt for correct formula and answer

1 pt for correct answer

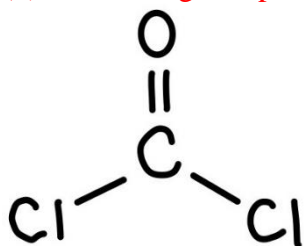
(-0.5 pt for incorrect s.f.; -0.5 pt for incorrect unit)

3. (8 pt) Determine the molecular shapes and hybridization types of the central atom for the following molecules: (a) NO_2^- , (b) COCl_2 , (c) H_3O^+ , and (d) ICl_4^- .

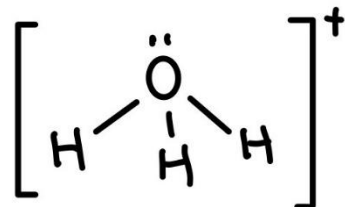
(a) NO_2^- : bend(1pt), sp^2 (1pt)



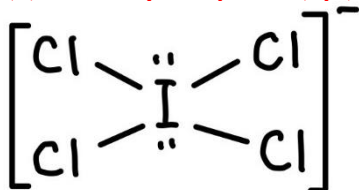
(b) COCl_2 : trigonal planar(1pt), sp^2 (1pt)



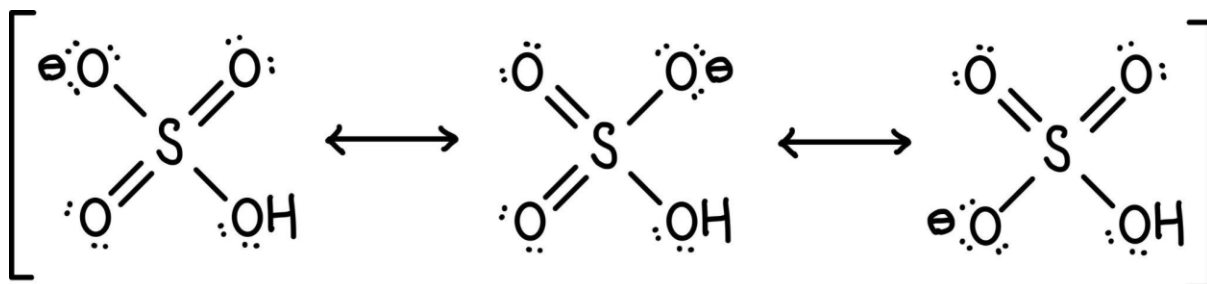
(c) H_3O^+ : trigonal pyramidal(1pt), sp^3 (1pt)



(d) ICl_4^- : square planar(1pt), d^2sp^3 (1pt)



4. (4 pt) Draw resonance structures of HSO_4^- ion.



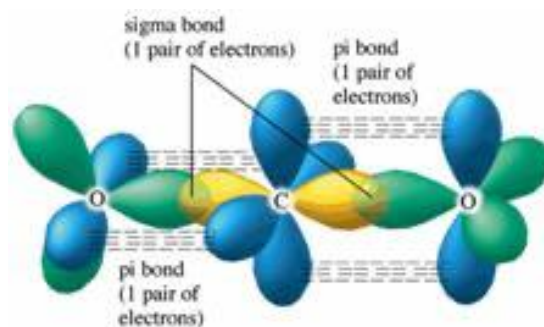
-1 pt for not labeling the charge

-2 pt for any missing resonance structures

-0.5 pt for minor mistakes (Ex: lone pairs, arrows, bondings)

(Maximum deduction: 4 pt)

5. (6 pt) Use valence bond theory and the hybridization concept to describe the chemical bonding in a carbon dioxide (CO_2) molecule.



VB theory:(1.5 pt each)

1. Carbon atom has 1 sigma-bond and 2 pi-bond
2. Each oxygen atom has 1 sigma-bond and 1 pi-bond

Hybridization concept: (1.5 pt each)

1. Carbon atom is sp hybridization with 2p orbitals remaining ($2p_y$ and $2p_z$ orbital)
2. Each oxygen atom is sp^2 hybridization with 2p orbital remaining ($2p_y$ for one oxygen and $2p_z$ for the other)

Optional:

1. According to the VSEPR model, the CO_2 molecule is linear
2. 2 pi-bonds are perpendicular to each other for they are constructed by side-by-side connection of $2p_y$ and $2p_z$ orbital

6. (6 pt) (a) Compare the relative bond energies of O_2 , O_2^+ , O_2^- , and O_2^{2-} using MO theory. (b) Which of these molecules are diamagnetic?

Bond order of each oxygen-related species:

$$\text{O}_2^+ = 2.5; \text{O}_2 = 2; \text{O}_2^- = 1.5; \text{O}_2^{2-} = 1$$

Because bond energy decreases within bond order, the bond energy:

$$\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}.$$

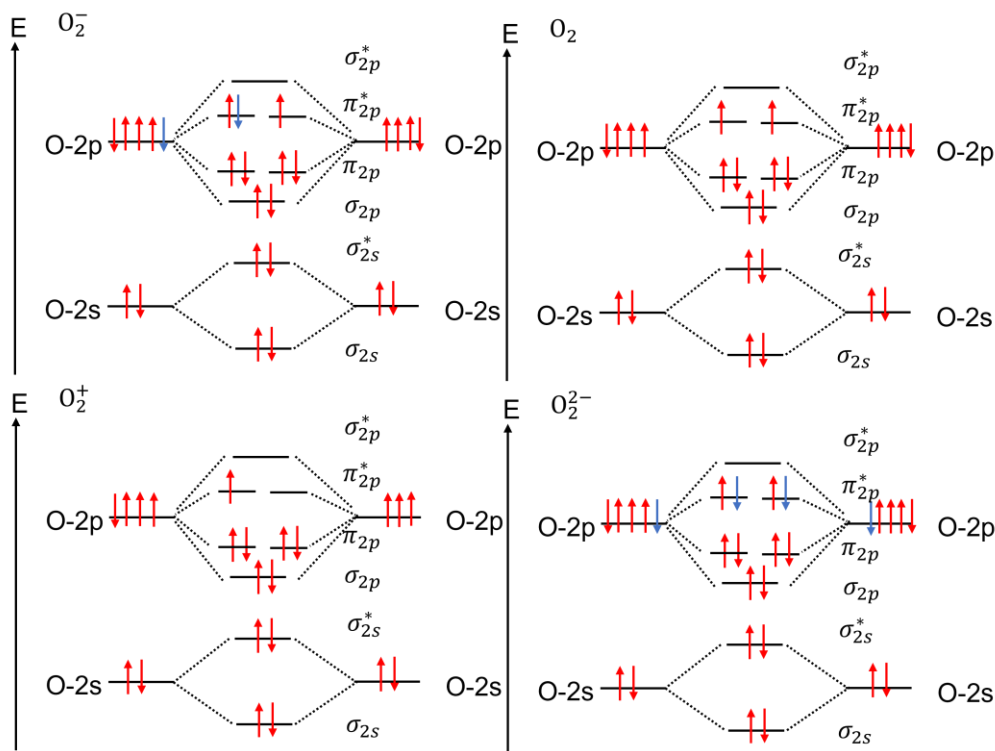
Diamagnetic refers to paired electrons, while paramagnetic fulfills the existence of unpaired electrons.

From the MO diagram of all the oxygen species, we can conclude that only O_2^{2-} is diamagnetic.

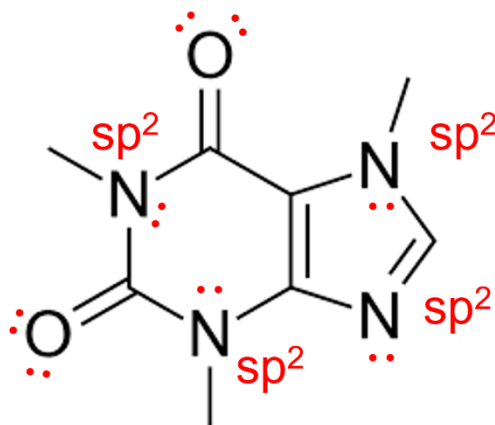
2pt bond order/ or drawing correct MO

2pt for bond energy

2 pt for correct species of diamagnetism



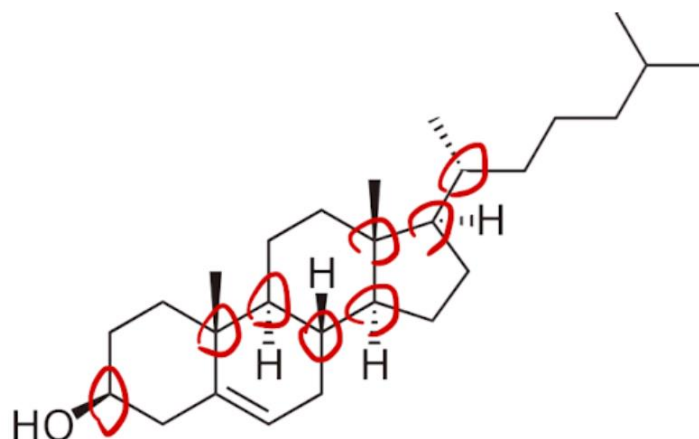
7. (8 pt) Caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) can be found in many beverages and food. (a) Draw the Lewis structure of caffeine, including lone electron pairs (you may use your Google friend). (b) How many σ bonds and π bonds exist in a caffeine molecule? (c) Label the hybridization types of the four nitrogen atoms in caffeine.



25 sigma-bonds, 7 pi-bonds (no deduction for "4 pi-bonds")

- 2pt for correct structure
- 1 pt for correct sigma, 1 pt for correct pi
- 1 pt for each hybridization of nitrogen atom

8. (4 pt) Draw the skeleton chemical structure of cholesterol ($C_{27}H_{46}O$, and yes, you may use your Google friend again). Label all the chiral centers in this molecule.

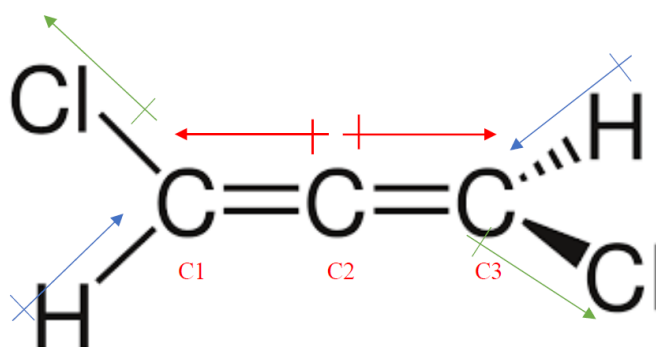


There are 8 chiral centers in total.

0.5 pt for each chiral center and atom direction

3 pt for wrong structure

9. (4 pt) Does this molecule have a non-zero dipole moment?



First, we can label the dipole moment of each bond as we described below.

(1) C-C bond dipole moment due to the inductive effect of Cl, which is labeled with red line.

(2) C-H bond dipole moment is labeled in blue.

(3) C-Cl bond dipole moment is labeled in green.

1pt for correct structure

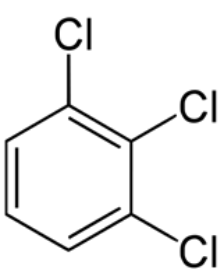
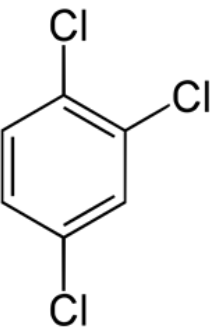
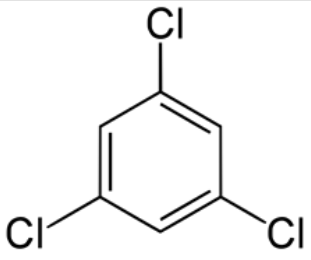
4pt for “polar”

We should know the structure of 1,3-dichloroallene, which is similar to **CO2** in Q8.

C1 carbon and C3 carbon are both sp^2 hybridization but left different p orbital (p_x , p_z respectively). The two planers made up with C1 and C3 respectively are perpendicular to

each other, hence, the dipole moment vector can't be deleted in the whole molecule. That is, this molecule is polar.

10. (4 pt) Arrange all the isomers of trichlorobenzene in the order of decreasing dipole moment.

	1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene	1,3,5-Trichlorobenzene
			
order of dipole moment	1	2	3(nonpolar)

0.5 pt for each answer & structure