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QUESTION 9
(8 points)

9. Explain each of the following observations in terms of the electronic structure and/or bonding of the compounds involved.

   (a) At ordinary conditions, HF (normal boiling point = 20°C) is a liquid, whereas HCl (normal boiling point = −114°C) is a gas.

   (b) Molecules of AsF_3 are polar, whereas molecules of AsF_5 are nonpolar.

   (c) The N–O bonds in the NO_2^- ion are equal in length, whereas they are unequal in HNO_2.

   (d) For sulfur, the fluorides SF_2, SF_4, and SF_6 are known to exist, whereas for oxygen only OF_2 is known to exist.

Scoring Guide

(a) Hydrogen bonding (or dipole -dipole attraction) in HF — ***1 point***
is greater than it is in HCl — ***1 point***

(Note: only 1 point earned if simply stated that HF has greater intermolecular forces than HCl)

(b) AsF_3 has a trigonal pyramid shape and bond dipoles do NOT cancel (or, asymmetric molecule) — ***1 point***

AsF_5 has a trigonal bipyramid shape and bond dipoles cancel (or, symmetric molecule) — ***1 point***

(Notes: explanation must refer to shape in order to earn point; 1 point earned if only correct Lewis structures are given)

(c) NO_2^- has resonance structures — ***1 point***

[:Ö=N̈–Ö:]$^{-1}$ ↔ [:Ö–N̈=Ö:]$^{-1}$

HNO_2 has no resonance structures

H–Ö–N̈=Ö:

OR, one N–O single bond, one N=O double bond — ***1 point***

(Note: 1 point earned if only correct Lewis structures, including resonance for NO_2^-, are given)

(d) Sulfur uses *d* orbitals (or expanded octet), — ***1 point***
oxygen has no *d* orbitals in its valence shell — ***1 point***

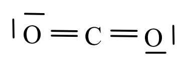
OR, Sulfur is a larger atom, can accommodate more bonds — ***2 points***

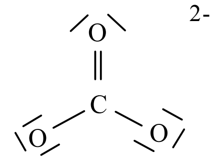
Question 8

8 points

(a) (i)

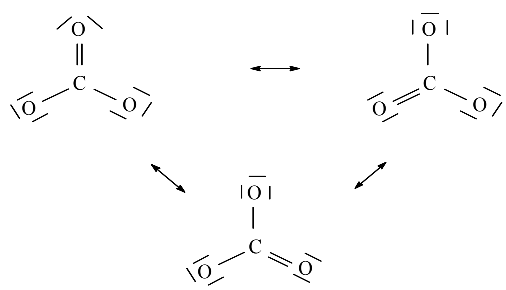
2 pts





- One point earned for each Lewis electron-dot structure
- Indication of lone pairs of electrons are required on each structure
- Resonance forms of CO_3^{2-} are not required

(ii) In CO_2, the C–O interactions are double bonds, **OR**, in CO_3^{2-} the C–O interactions are resonance forms (or figures below.) ***1 pt***

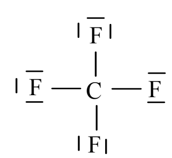


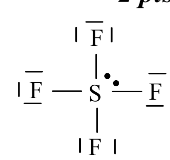
The carbon-oxygen bond length is greater in the resonance forms than in the double bonds. ***1 pt***

- 1st point earned for indicating double bonds are present in CO_2 **OR** resonance occurs in CO_3^{2-}
- 2nd point earned for **BOTH** of the above **AND** indicating the relative lengths of the bond types

(b) (i)

2 pts



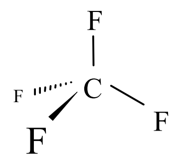


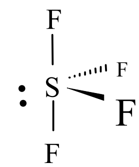
- One point earned for each Lewis electron-dot structure
- Lone pairs of electrons are required on each structure

Question 8 (cont.)

(ii) CF_4 has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule. ***1 pt***

With five pairs of electrons around the central S atom, SF_4 exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar. ***1 pt***





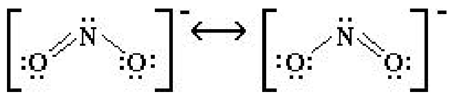
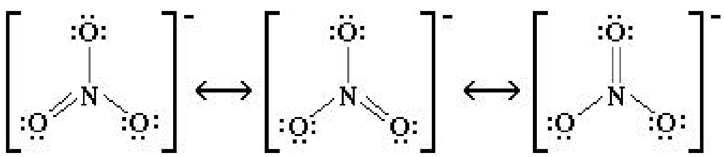
- One point earned for each molecule for proper geometry and explanation

Question 6

10 points

Using principles of chemical bonding and molecular geometry, explain each of the following observations. Lewis electron-dot diagrams and sketches of molecules may be helpful as part of your explanations. For each observation, your answer must include references to both substances.

(a) The bonds in nitrite ion, NO_2^-, are shorter than the bonds in nitrate ion, NO_3^-.

 According to the Lewis electron-dot diagram, two resonance structures are required to represent the bonding in the NO_2^- ion. The effective number of bonds between N and O is 1.5.	1 point earned for the difference in the effective number of bonds in both ions
 Three resonance structures are required to represent the bonding in the NO_3^- ion. The effective number of bonds between N and O is 1.33. The greater the effective number of bonds, the shorter the N–O bond length.	1 point earned for relating the effective number of bonds to bond length

(b) The CH_2F_2 molecule is polar, whereas the CF_4 molecule is not.

The molecular geometry in both CH_2F_2 and CF_4 is tetrahedral (or the same). The C-F bond is polar. In CF_4, the molecular geometry arranges the C-F dipoles so that they cancel out and the molecule is nonpolar. The C-H bond is less polar than the C-F bond. The two C-H dipoles do not cancel the two C-F dipoles in CH_2F_2.	1 point earned for discussing the similarity in molecular geometry 1 point earned for discussing the relationship between molecular geometry and the C-H and C-F bond dipoles

Question 6 (cont'd.)

(c) The atoms in a C_2H_4 molecule are located in a single plane, whereas those in a C_2H_6 molecule are not.

The carbon atoms in C_2H_4 have a molecular geometry around each carbon atom that is trigonal planar (AX_3), so all six atoms are in the same plane. The carbon atoms in C_2H_6 have a molecular geometry that is tetrahedral (AX_4), so the atoms are not all in the same plane. **OR** The carbon-carbon double bond in C_2H_4 results in a planar molecule whereas the carbon-carbon single bond in C_2H_6 results in a non-planar (tetrahedral) site at each carbon atom.	1 point earned for the bonding of the carbon atoms 1 point earned for the structure

(d) The shape of a PF_5 molecule differs from that of an IF_5 molecule.

In PF_5, the molecular geometry is trigonal bipyramidal because the phosphorus atom has five bonding pairs of electrons and no lone pairs of electrons. IF_5 has square pyramdal molecular geometry. The central iodine atom has five bonding pairs of electrons and one lone pair of electrons. The presence of the additional lone pair of electrons on the central iodine atom means the molecular geometry is different.	1 point earned for discussing the difference made by the lone pair of electrons in IF_5 and how it affects the geometry of the two molecules

(e) $HClO_3$ is a stronger acid than $HClO$.

According to the formula for HOCl and $HOClO_2$, there are two additional terminal, electronegative oxygen atoms attached to the central chlorine atom. These additional terminal oxygen atom stabilize the negative charge on the anion ClO_3^- compared to ClO^-. The result is to reduce the electrostatic attraction between the H^+ and ClO_x^-. **OR** The two additional terminal electronegative O atoms bonded to the chlorine atom of ClO_3^- pull electron density away from the central chlorine atom. The net result is to weaken the H-O bond. Since HOCl has no additional terminal O atoms, its H-O bond is stronger. The weaker the H-O bond, the stronger the acid.	1 point earned for discussing the importance of the electronegativity of the terminal oxygen atoms in the two structures and/or the enhanced stability of the chlorate vs. the hypochlorite ion

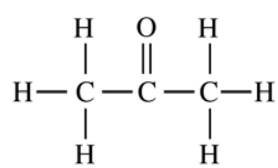
Question 8

Compound Name	Compound Formula	ΔH°_{vap} (kJ mol^{-1})
Propane	$CH_3CH_2CH_3$	19.0
Propanone	CH_3COCH_3	32.0
1-propanol	$CH_3CH_2CH_2OH$	47.3

8. Using the information in the table above, answer the following questions about organic compounds.

(a) For propanone,

(i) draw the complete structural formula (showing all atoms and bonds);

	1 point for complete and correct structural formula

(ii) predict the approximate carbon-to-carbon-to-carbon bond angle.

The C – C – C bond angle is 120°	1 point for bond angle

(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization, ΔH°_{vap}. (You must include specific information about both compounds in each pair.)

(i) Propane and propanone

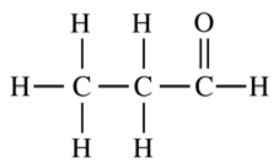
The intermolecular attractive forces in propane are dispersion forces only. The IMFs in propanone are dispersion and dipole-dipole. Since the intermolecular attractive forces differ in the two substances, the enthalpy of vaporization will differ.	1 point for correctly identifying the IMFs for each substance

Question 8 (cont'd.)

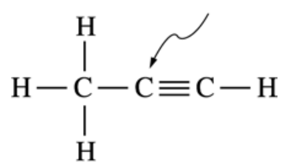
(ii) Propanone and 1-propanol

The intermolecular attractive forces in 1-propanol are dispersion forces and hydrogen-bonding. The IMFs in propanone are dispersion and dipole-dipole. Since the intermolecular attractive forces differ in the two substances, the enthalpy of vaporization will differ.	1 point for correctly identifying the IMFs for each substance

(c) Draw the complete structural formula for an isomer of the molecule you drew in part (a) (i).

	1 point for correct, complete structural formula

(d) Given the structural formula for propyne below,



(i) indicate the hybridization of the carbon atom indicated by the arrow in the structure above;

sp hybridization	1 point for correct hybridization

(ii) indicate the total number of sigma (σ) bonds and the total number of pi (π) bonds in the molecule.

6 sigma bonds 2 pi bonds	1 point for correct number of sigma bonds 1 point for correct number of pi bonds