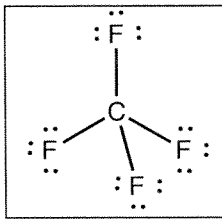
NMSI SUPER PROBLEM

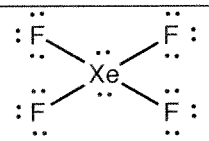
Answer the following questions about the molecules and reactions containing fluorine atoms.

(a) Draw the Lewis structures for

i. CF_4

	**1 point** for the correct Lewis structure; atoms must show lone pair electrons if present

ii. XeF_4.

	**1 point** for the correct Lewis structure; atoms must show lone pair electrons if present

(b) Although CF_4 and XeF_4 *both* have the 4 atoms of fluorine around the central atom they have different molecular shapes. Explain this difference. Be sure to state the correct molecular geometry of both molecules in your explanation.

CF_4 molecules are tetrahedral in their molecular geometry whereas molecules of XeF_4 are square planar. Although they both have four fluorine atoms the Xe atom has 2 sets of lone pair electrons – or 6 regions of electron density and the C atom only has the 4 regions of electron density – it has no lone pairs, therefore they will have different molecular geometries.	**1 point** for correct explanation **1 point** for stating both molecular geometries

(c) Identify the hybridization about the C atom in CF_4.

sp^3	**1 point** for the correct hybridization, consistent with part (a)

(d) Indicate whether molecules of XeF_4 are polar or nonpolar. Justify your answer.

Nonpolar; because the molecule has an equal distribution of electron density there is no NET DIPOLE moment as the individual dipoles cancel each other out due to the square planar shape.	**1 point** for the correct polarity with justification

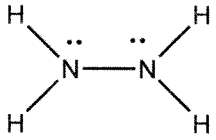
(e) Explain why nitrogen only forms the fluoride NF_3 but arsenic forms both AsF_3 and AsF_5.

Nitrogen can't form an expanded octet since it lacks the *d* orbitals which are required to form NF_5 Arsenic has *d* orbitals that can allow for an expanded octet.	**1 point** for the lack of *d* orbitals **1 point** for stating that As has empty d orbitals available for electrons. (or similar correct argument).

Fluorine reacts with hydrazine, N_2H_4, as shown in the reaction below at 25°C and 1 atm.

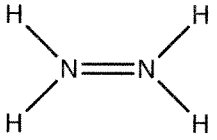
$$N_2H_4(\ell) + 2\ F_2(g) \rightarrow N_2(g)\ +\ 4HF(g) \quad \Delta H°_{rxn} = -1169\ \text{kJ mol}_{rxn}^{-1}$$

(f) Determine the number of *both* sigma and pi bonds in N_2H_4. The Lewis structure for N_2H_4 is shown below.



5 sigma bonds; 0 pi bonds	**1 point** for correct number of both sigma and pi bonds

(g) A student drew the following competing structure for hydrazine. Use the concept of formal charge to support which Lewis diagram best represent a molecule of hydrazine.



In the first Lewis diagram of hydrazine the formal charge on the Nitrogen atom is zero (5–2–3). In the Lewis diagram of hydrazine with the double bond the formal charge on the Nitrogen atom is +1 (5–0–4). Thus the first (with lone electron pairs on the nitrogen atoms) Lewis diagram best represents a molecule of hydrazine.	**1 point** for selecting the first Lewis diagram as the best representation of hydrazine with correct justification using formal charge.

(h) Using the table of bond enthalpies below, calculate the enthalpy of an N–H bond.

Bonds	Bond Enthalpies (kJ/mol)
N—N	160
N=N	418
N≡N	941
F—H	565
F—F	154
N—H	???

$\Delta H°_{rxn}$ = Sum of Bonds Broken – Sum of Bonds Formed −1169 kJ/mol =[160 + 4(BE_{N-H}) + 2(154)]- [(941) + 4(565)] 1564 kJ/mol = 4(BE_{N-H}) BE_{N-H} = 391 kJ/mol	**1 point** for correct sign for the enthalpy of reaction **1 point** for correct substitution **1 point** for correct N–H bond energy

(i) Is the average kinetic energy of the nitrogen gas, N_2, greater than, less than, or equal to the average kinetic energy of hydrogen fluoride gas, HF, when both are at the same temperature? Justify your answer.

Since both gases are at the same temperature, the average kinetic energy of N_2 and HF is the same.	**1 point** for stating both substances have the same average kinetic energy because they are at the same temperature; or similar justification.

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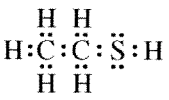
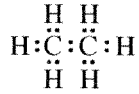
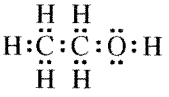
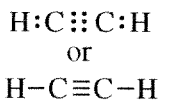
(8 points)

Use the information in the table below to respond to the statements and questions that follow. Your answers should be in terms of principles of molecular structure and intermolecular forces.

Compound	Formula	Lewis Electron-Dot Diagram
Ethanethiol	CH_3CH_2SH	
Ethane	CH_3CH_3	
Ethanol	CH_3CH_2OH	
Ethyne	C_2H_2	 or

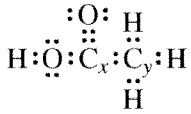
(a) Draw the complete Lewis electron-dot diagram for ethyne in the appropriate cell in the table above.

See the lower right cell in the table above.	One point is earned for the correct Lewis structure.

(b) Which of the four molecules contains the shortest carbon-to-carbon bond? Explain.

Ethyne, which contains a triple bond, has the shortest C-to-C bond. The other molecules have single C-to-C bonds, and triple bonds are shorter than single bonds.	One point is earned for the correct choice. One point is earned for the correct explanation.

(c) A Lewis electron-dot diagram of a molecule of ethanoic acid is given below. The carbon atoms in the molecule are labeled x and y, respectively.



Identify the geometry of the arrangement of atoms bonded to each of the following.

(i) Carbon x

Trigonal planar	One point is earned for the correct geometry.

(ii) Carbon y

Distorted tetrahedral, tetrahedral or trigonal pyramidal	One point is earned for the correct geometry.

(d) Energy is required to boil ethanol. Consider the statement "As ethanol boils, energy goes into breaking C–C bonds, C–H bonds, C–O bonds, and O–H bonds." Is the statement true or false? Justify your answer.

The statement is false. All of the bonds described are intramolecular; these bonds are not broken during vaporization. When ethanol boils, the added energy overcomes intermolecular, not intramolecular, forces.	One point is earned for the correct choice with justification.

(e) Identify a compound from the table above that is nonpolar. Justify your answer.

Either ethane or ethyne may be identified as nonpolar. The ethane/ethyne molecule is nonpolar because all of the bond dipoles in the molecule cancel. ***OR*** The ethane/ethyne molecule is nonpolar because the molecule is symmetric. Note: Explanation must refer to the shape of the molecule. Statements such as: "all hydrocarbons are nonpolar', "the carbons are surrounded by hydrogens" or "there are no lone pairs" do not earn this point.	One point is earned for a correct choice with justification.

(f) Ethanol is completely soluble in water, whereas ethanethiol has limited solubility in water. Account for the difference in solubilities between the two compounds in terms of intermolecular forces.

Ethanol is able to form strong hydrogen bonds with water whereas ethanethiol does not have similar capability. The formation of hydrogen bonds increases the attraction between molecules of ethanol and molecules of water, making them more soluble in each other. Note: The answer must clearly focus on the solute-solvent interaction. Just the mention of hydrogen bonding does not earn the point.	One point is earned for the correct explanation.

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(2 points)

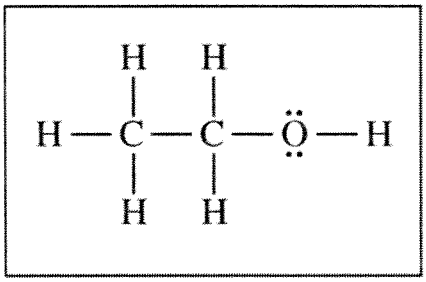
Answer the following questions using principles of molecular structure and intermolecular forces.

Compound	Empirical Formula	Solubility in Water	Boiling Point (°C)
1	C_2H_6O	Slightly soluble	−24
2	C_2H_6O	Soluble	78

Compounds 1 and 2 in the data table above have the same empirical formula, but they have different physical properties.

(a) The skeletal structure for one of the two compounds is shown below in Box X.

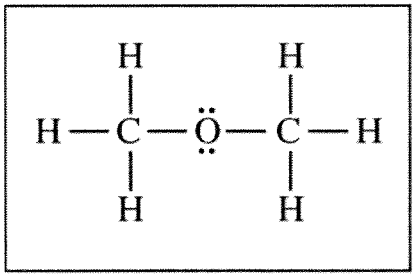
(i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.



Box X

1 point is earned for a correct Lewis diagram.

(ii) In Box Y below, draw the complete Lewis electron-dot diagram for the other compound, which is a structural isomer of the compound represented in Box X. Include any lone (nonbonding) pairs of electrons.



Box Y

1 point is earned for a correct Lewis diagram.

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(3 points)

A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

(a) Using the data in the table below, calculate the value, in kJ/mol_{rxn}, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

$\Delta H°$ = enthalpy of bonds broken – enthalpy of bonds formed $\Delta H° = [5(\Delta H_{C\text{-}H}) + (\Delta H_{C\text{-}N}) + (\Delta H_{C\text{-}C}) + 2(\Delta H_{N\text{-}H})] -$ $[4(\Delta H_{C\text{-}H}) + (\Delta H_{C=C}) + 3(\Delta H_{N\text{-}H})]$ $= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49\ kJ/mol_{rxn}$ **OR** $\Delta H° = [(\Delta H_{C\text{-}H}) + (\Delta H_{C\text{-}N}) + (\Delta H_{C\text{-}C})] - [(\Delta H_{C=C}) + (\Delta H_{N\text{-}H})]$ $= [413 + 293 + 348]\ kJ/mol - [614 + 391]\ kJ/mol = 49\ kJ/mol_{rxn}$	1 point is earned for the correct bond count and use of values from table. 1 point is earned for the correct setup in terms of bonds broken minus bonds formed and calculated $\Delta H°$.

(b) Based on your answer to part (a), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive $\Delta H°$.	1 point is earned for the correct choice with explanation.

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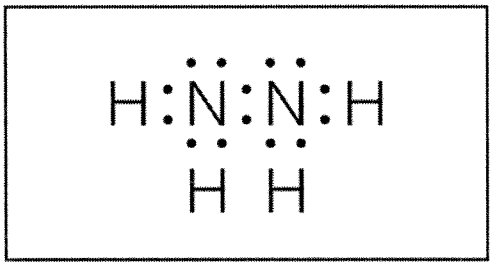
4 Points

Hydrazine is an inorganic compound with the formula N_2H_4.

(a) In the box below, complete the Lewis electron-dot diagram for the N_2H_4 molecule by drawing in all the electron pairs.



The correct Lewis diagram has single bonds between each pair of atoms and a lone pair of electrons on each N atom (a total of 14 e^-).	1 point is earned for the correct Lewis diagram.

(b) On the basis of the diagram you completed in part (a), do all six atoms in the N_2H_4 molecule lie in the same plane? Explain.

No, they do not. The molecular geometry surrounding both nitrogen atoms is trigonal pyramidal. Therefore the molecule as a whole cannot have all the atoms in the same plane.	1 point is earned for a correct answer with a valid explanation.

N_2H_4 reacts in air according to the equation below.

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(g) \qquad \Delta H^\circ = -534\ \text{kJ mol}^{-1}$$

(e) Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

The reaction is an oxidation-reduction reaction. The oxidation state of N changes from –2 to 0 while that of O changes from 0 to –2.	1 point is earned for the correct choice with a valid justification.

(g) Indicate whether the statement written in the box below is true or false. Justify your answer.

The large negative ΔH° for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

The statement is false on two counts. First, energy is released not when bonds are broken, but rather when they are formed. Second, the bonds in the reactants are relatively weak compared to the bonds in the products.	1 point is earned for correctly identifying the statement as false along with a valid justification.

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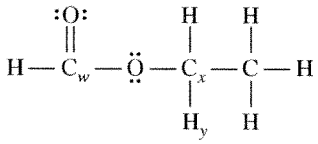
(3points)

Use principles of molecular structure, intermolecular forces, and kinetic molecular theory to answer the following questions.

(a) A complete Lewis electron-dot diagram of a molecule of ethyl methanoate is given below.



(i) Identify the hybridization of the valence electrons of the carbon atom labeled C_w.

sp^2	1 point is earned for the correct answer.

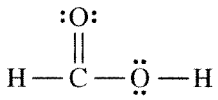
(ii) Estimate the numerical value of the H_y–C_x–O bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

The C_x is the central atom in a tetrahedral arrangment of bonding electron pairs; thus the angle would be approximately109.5°.	1 point is earned for the correct angle with an appropriate explanation.

(b) Ethyl methanoate, CH_3CH_2OCHO, is synthesized in the laboratory from ethanol, C_2H_5OH, and methanoic acid, $HCOOH$, as represented by the following equation.

$$C_2H_5OH(l) + HCOOH(l) \rightleftarrows CH_3CH_2OCHO(l) + H_2O(l)$$

(i) In the box below, draw the complete Lewis electron-dot diagram of a methanoic acid molecule.

	1 point is earned for a correct diagram.