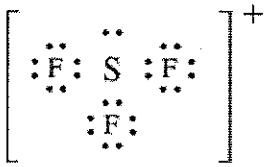
Question 7

7. Answer the following questions about the structures of ions that contain only sulfur and fluorine.

(a) The compounds SF_4 and BF_3 react to form an ionic compound according to the following equation.

$$SF_4 + BF_3 \rightarrow SF_3BF_4$$

(i) Draw a complete Lewis structure for the SF_3^+ cation in SF_3BF_4.

	One point is earned for the correct Lewis structure (the structure must include lone pairs of electrons, which may be represented as dashes).

(ii) Identify the type of hybridization exhibited by sulfur in the SF_3^+ cation.

sp^3	One point is earned for the correct hybridization.

(iii) Identify the geometry of the SF_3^+ cation that is consistent with the Lewis structure drawn in part (a)(i).

Trigonal pyramidal	One point is earned for the correct shape.

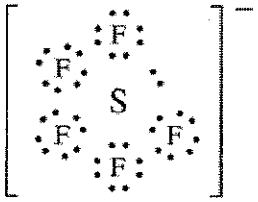
(iv) Predict whether the F–S–F bond angle in the SF_3^+ cation is larger than, equal to, or smaller than 109.5°. Justify your answer.

The F–S–F bond angle in the SF_3^+ cation is expected to be slightly <u>smaller</u> than 109.5° because the repulsion between the nonbonding pair of electrons and the S–F bonding pairs of electrons "squeezes" the F–S–F bond angles together slightly.	One point is earned for stating that the angle is smaller, with justification.

(b) The compounds SF_4 and CsF react to form an ionic compound according to the following equation.

$$SF_4 + CsF \rightarrow CsSF_5$$

(i) Draw a complete Lewis structure for the SF_5^- anion in $CsSF_5$.

	One point is earned for the correct Lewis structure (the structure must include lone pairs of electrons, which may be represented as dashes).

(ii) Identify the type of hybridization exhibited by sulfur in the SF_5^- anion.

sp^3d^2	One point is earned for the correct hybridization.

(iii) Identify the geometry of the SF_5^- anion that is consistent with the Lewis structure drawn in part (b)(i).

Square pyramidal	One point is earned for the correct shape.

(iv) Identify the oxidation number of sulfur in the compound $CsSF_5$.

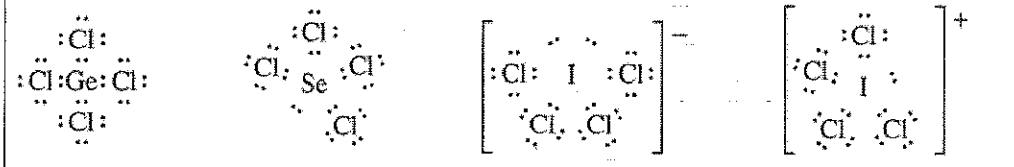
+4	One point is earned for the correct oxidation number.

Question 6

$GeCl_4$ $SeCl_4$ ICl_4^- ICl_4^+

6. The species represented above all have the same number of chlorine atoms attached to the central atom.

(a) Draw the Lewis structure (electron-dot diagram) of each of the four species. Show all valence electrons in your structures.

	One point is earned for each correct structure.

(b) On the basis of the Lewis structures drawn in part (a), answer the following questions about the particular species indicated.

(i) What is the $Cl-Ge-Cl$ bond angle in $GeCl_4$?

109.5°	One point is earned for the correct angle.

(ii) Is $SeCl_4$ polar? Explain.

Yes. The $SeCl_4$ molecule is polar because the lone pair of nonbonding electrons in the valence shell of the selenium atom interacts with the bonding pairs of electrons, causing a spatial asymmetry of the dipole moments of the polar Se-Cl bonds. The result is a $SeCl_4$ molecule with a net dipole moment.	One point is earned for the correct answer.

(iii) What is the hybridization of the I atom in ICl_4^- ?

d^2sp^3 or sp^3d^2	One point is earned for the correct hybridization.

(iv) What is the geometric shape formed by the atoms in ICl_4^+ ?

See-saw (or distorted tetrahedral or disphenoidal)	One point is earned for the correct shape.

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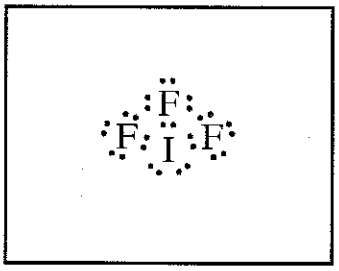
Question 6

Answer the following questions, which pertain to binary compounds.

(a) In the box provided below, draw a complete Lewis electron-dot diagram for the IF_3 molecule.

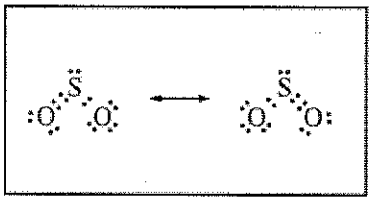


One point is earned for a correct Lewis diagram (can be done with dots or lines).

(b) On the basis of the Lewis electron-dot diagram that you drew in part (a), predict the molecular geometry of the IF_3 molecule.

T-shaped	One point is earned for the molecular geometry consistent with the Lewis diagram in part (a).

(c) In the SO_2 molecule, both of the bonds between sulfur and oxygen have the same length. Explain this observation, supporting your explanation by drawing in the box below a Lewis electron-dot diagram (or diagrams) for the SO_2 molecule.



One point is earned for a correct diagram (can be done with dots or lines). One point is earned for some indication or discussion of resonance (but the point is not earned for a description of resonance as a dynamic process). **OR**	
$\overline{\underline{O}}=\overline{\underline{S}}=\overline{\underline{O}}$ The bonds are the same length because they are both double bonds.	One point is earned for a correct diagram (can be done with dots or lines). One point is earned for stating that both bonds are double bonds.

Question 6 (continued)

(d) On the basis of your Lewis electron-dot diagram(s) in part (c), identify the hybridization of the sulfur atom in the SO_2 molecule.

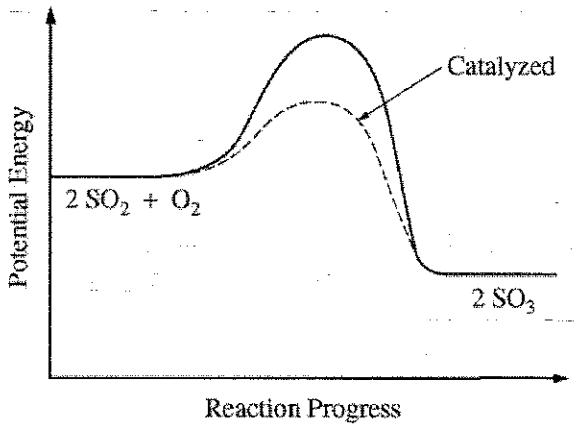
sp^2	One point is earned for hybridization consistent with part (c).

The reaction between $SO_2(g)$ and $O_2(g)$ to form $SO_3(g)$ is represented below.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$$

The reaction is exothermic. The reaction is slow at 25°C; however, a catalyst will cause the reaction to proceed faster.

(e) Using the axes provided below, draw the complete potential-energy diagram for both the catalyzed and uncatalyzed reactions. Clearly label the curve that represents the catalyzed reaction.



One point is earned for an uncatalyzed reaction curve that must show that $E_a > 0$ and $\Delta H < 0$.

One point is earned for a catalyzed reaction curve that must show $E_a <$ uncatalyzed E_a, must be clearly labeled, and must begin and end at the same energies as the uncatalyzed curve.

Question 6 (continued)

(f) Predict how the ratio of the equilibrium pressures, $\frac{P_{SO_2}}{P_{SO_3}}$, would change when the temperature of the uncatalyzed reaction mixture is increased. Justify your prediction.

The ratio $\frac{P_{SO_2}}{P_{SO_3}}$ would increase as the temperature increases. Because the reaction is exothermic ($\Delta H < 0$), as the temperature is raised the reaction shifts to the left.	One point is earned for the correct answer and explanation.

(g) How would the presence of a catalyst affect the change in the ratio described in part (f)? Explain.

The catalyst would not affect the value of the two equilibrium ratios but would increase the rate of the shifting of the system to the new equilibrium position. The catalyst does this by providing an alternate path with a lower activation energy.	One point is earned for the correct answer and explanation.

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Question 5

Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy ($kJ\ mol^{-1}$)
F	1,681.0
O	1,313.9
Xe	?

(a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 $kJ\ mol^{-1}$.

$F(g) \rightarrow F^+(g) + e^-$	One point is earned for the correct equation. (Phase designations are not required.)

(b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)

In both cases the electron removed is from the same energy level ($2p$), but fluorine has a greater effective nuclear charge due to one more proton in its nucleus (the electrons are held more tightly and thus take more energy to remove).	One point is earned for recognizing that the effective nuclear charge of F is greater than that of O.

(c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

The first ionization energy of Xe should be less than the first ionization energy of F. To ionize the F atom, an electron is removed from a $2p$ orbital. To ionize the Xe atom, an electron must be removed from a $5p$ orbital. The $5p$ is a higher energy level and is farther from the nucleus than $2p$, hence it takes less energy to remove an electron from Xe.	One point is earned for a prediction based on size and/or energy level.

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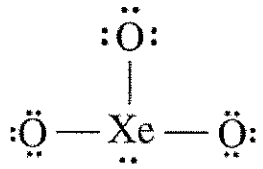
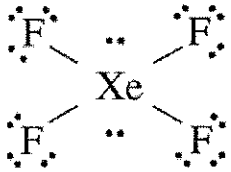
Question 5 (continued)

(d) Xenon can react with oxygen and fluorine to form compounds such as XeO_3 and XeF_4. In the boxes provided, draw the complete Lewis electron-dot diagram for each of the molecules represented below.

XeO_3	XeF_4	
		One point is earned for each correct Lewis electron-dot diagram. Omission of lone pairs of electrons on the O or F atoms results in a one-time, 1-point deduction.

(e) On the basis of the Lewis electron-dot diagrams you drew for part (d), predict the following:

(i) The geometric shape of the XeO_3 molecule

Trigonal pyramidal	One point is earned for a shape that is consistent with the Lewis electron-dot diagram.

(ii) The hybridization of the valence orbitals of xenon in XeF_4

sp^3d^2	One point is earned for the hybridization consistent with the Lewis electron-dot diagram.

(f) Predict whether the XeO_3 molecule is polar or nonpolar. Justify your prediction.

The XeO_3 molecule would be polar because it contains three polar Xe–O bonds that are asymmetrically arranged around the central Xe atom (i.e., the bond dipoles do not cancel but add to a net molecular dipole with the Xe atom at the positive end).	One point is earned for the answer that is consistent with the shape indicated in part (e)(i). One point is earned for an explanation correctly related to the shape in part (e)(i).

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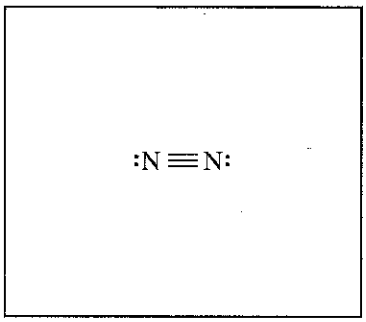
Question 5 (9 points)

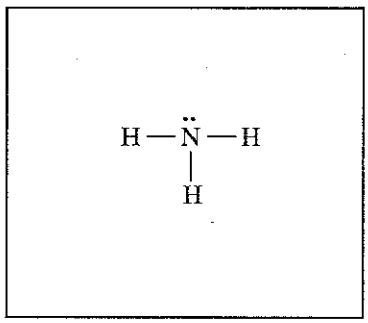
Answer the following questions about nitrogen, hydrogen, and ammonia.

(a) In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

N_2



NH_3



The correct structures are shown in the boxes above.	Two points are earned for the correct Lewis electron-dot diagrams (1 point each).

(b) Calculate the standard free-energy change, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$$N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g) \qquad \Delta G°_{298} = -34\ \text{kJ mol}^{-1}$$

$12.0\ \text{g}\ H_2 \times \frac{1\ \text{mol}\ H_2}{2.0\ \text{g}\ H_2} \times \frac{1\ \text{mol reaction}}{3\ \text{mol}\ H_2} \times \frac{-34\ \text{kJ}}{1\ \text{mol reaction}} = \mathbf{-68\ kJ}$	One point is earned for the correct stoichiometry. One point is earned for the correct answer.

(c) Given that $\Delta H°_{298}$ for the reaction is $-92.2\ \text{kJ mol}^{-1}$, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$\Delta H°_{298} = \Sigma$ (bond energy of the reactants) $- \Sigma$ (bond energy of the products) Based on the equation above, for $\Delta H°_{298}$ to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants. **OR** More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.	One point is earned for the correct answer with the correct equation and explanation.

Question 5 (continued)

(d) The value of the standard entropy change, ΔS°_{298}, for the reaction is -199 J mol^{-1}K^{-1}. Explain why the value of ΔS°_{298} is negative.

All of the reactants and products in the reaction are in the gas phase, so the sign of the entropy change will depend on the number of moles of particles in the reactants and products. There are more moles of reactants (four) compared with moles of products (two), so there is a greater number of microstates in the reactants than in the products. Therefore the entropy decreases as the reaction proceeds (fewer possible microstates), and the sign of the entropy change is negative.	One point is earned for the correct explanation.

(e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ As the temperature increases $\lvert T\Delta S^\circ\rvert$ will at some point exceed $\lvert\Delta H^\circ\rvert$. Because both ΔH° and ΔS° are negative, the sign of ΔG° will then change from negative to positive.	One point is earned for the correct explanation.

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

Low temperatures: The reaction is exothermic. By Le Chatelier's principle, decreasing the temperature drives the reaction to the right to produce more heat energy, and thus more ammonia is produced.	One point is earned for explaining increased yield at low temperatures.
High pressures: For this reaction, higher pressure is achieved by decreasing the volume of the container. As pressure increases, the reaction equilibrium shifts in the direction that reduces the total number of particles (by Le Chatelier's principle). In this case, the product has fewer moles of particles than the reactants; thus product would be favored. Higher pressure therefore results in an increase in the amount of ammonia.	One point is earned for explaining increased yield at high pressures.

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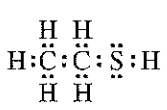
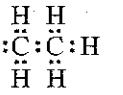
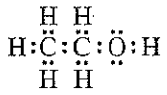
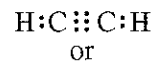
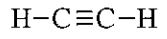
Question 5
(8 points)

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.

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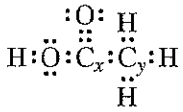
Question 5 (continued)

(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.

Question 5 (continued)

(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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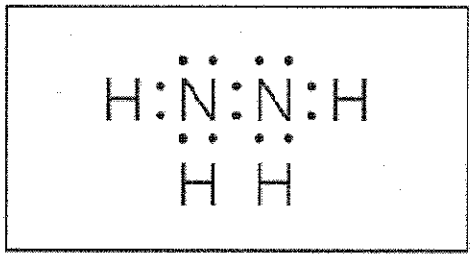
2011 SCORING GUIDELINES

Question 5

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.

(c) The normal boiling point of N_2H_4 is 114°C, whereas the normal boiling point of C_2H_6 is −89°C. Explain, in terms of the intermolecular forces present in each liquid, why the boiling point of N_2H_4 is so much higher than that of C_2H_6.

N_2H_4 is a polar molecule with London dispersion forces, dipole-dipole forces, and hydrogen bonding between molecules, whereas C_2H_6 is nonpolar and only has London dispersion forces between molecules. It takes more energy to overcome the stronger IMFs in hydrazine, resulting in a higher boiling point.	1 point is earned for correct reference to the two different types of IMFs. 1 point is earned for a valid explanation based on the relative strengths of the IMFs.

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Question 5 (continued)

(d) Write a balanced chemical equation for the reaction between N_2H_4 and H_2O that explains why a solution of hydrazine in water has a pH greater than 7.

$N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$	1 point is earned for a valid equation.

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.

(f) Predict the sign of the entropy change, ΔS, for the reaction. Justify your prediction.

The entropy change for the reaction is expected to be positive. There are three moles of gas produced from one mole of liquid and one mole of gas. The net increase of two moles of gas results in a greater entropy of products compared to the entropy of reactants.	1 point is earned for the correct prediction 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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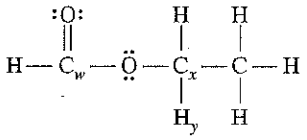
2011 SCORING GUIDELINES (Form B)

Question 6
(8 points)

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.

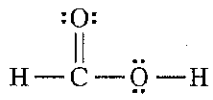
(ii) Estimate the numerical value of the H_y–C_x–O bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

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.

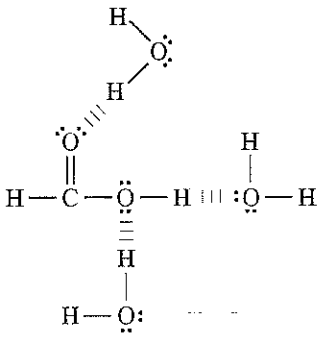
$$C_2H_5OH(l) + HCOOH(l) \rightleftarrows CH_3CH_2OCHO(l) + H_2O(l)$$

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

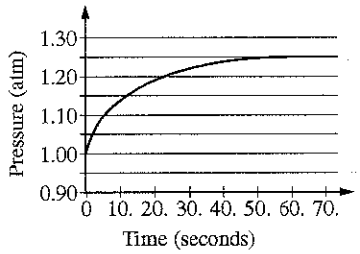
	1 point is earned for a correct diagram.

Question 6 (continued)

(ii) In the box below, draw the complete Lewis electron-dot diagrams of a methanoic acid molecule and a water molecule in an orientation that allows a hydrogen bond to form between them.

 Hydrogen Bonding Between Methanoic Acid and Water	1 point is earned for a diagram showing a reasonable orientation between a methanoic acid molecule and a water molecule.

(c) A small amount of liquid ethyl methanoate (boiling point 54°C) was placed in a rigid closed 2.0 L container containing argon gas at an initial pressure of 1.00 atm and a temperature of 20°C. The pressure in the container was monitored for 70. seconds after the ethyl methanoate was added, and the data in the graph below were obtained. It was observed that some liquid ethyl methanoate remained in the flask after 70. seconds. (Assume that the volume of the remaining liquid is negligible compared to the total volume of the container.)



(i) Explain why the pressure in the flask increased during the first 60. seconds.

Some of the liquid ethyl methanoate is going into the gas (vapor) phase.	1 point is earned for the correct explanation.

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Question 6 (continued)

(ii) Explain, in terms of processes occurring at the molecular level, why the pressure in the flask remained constant after 60. seconds.

At the equilibrium vapor pressure, the rate of molecules passing from the liquid to the gas phase (vaporizing) equals the rate of gas phase molecules passing into the liquid phase (condensing).	1 point is earned for the correct explanation.

(iii) What is the value of the partial pressure of ethyl methanoate vapor in the container at 60. seconds?

1.25 atm – 1.00 atm = 0.25 atm	1 point is earned for the correct answer.

(iv) After 80. seconds, additional liquid ethyl methanoate is added to the container at 20°C. Does the partial pressure of the ethyl methanoate vapor in the container increase, decrease, or stay the same? Explain. (Assume that the volume of the additional liquid ethyl methanoate in the container is negligible compared to the total volume of the container.)

The partial pressure of the vapor stays the same because the equilibrium vapor pressure for 20°C has already been reached. Because the temperature remains constant, the vapor pressure would remain unchanged.	1 point is earned for the correct answer with an explanation.