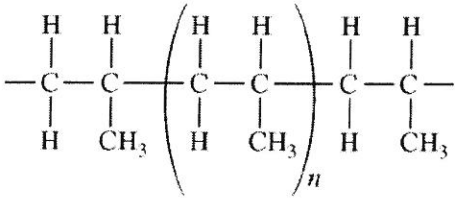
Key

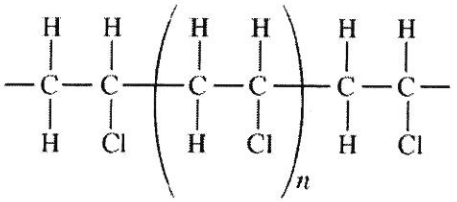
AP® CHEMISTRY
2014 SCORING GUIDELINES

Question 6
(4 points)

A student places a mixture of plastic beads consisting of polypropylene (PP) and polyvinyl chloride (PVC) in a 1.0 L beaker containing distilled water. After stirring the contents of the beaker vigorously, the student observes that the beads of one type of plastic sink to the bottom of the beaker and the beads of the other type of plastic float on the water. The chemical structures of PP and PVC are represented by the diagrams below, which show segments of each polymer.



PP

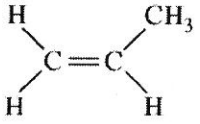


PVC

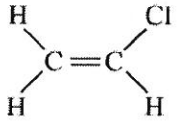
(a) Given that the spacing between polymer chains in PP and PVC is similar, the beads that sink are made of which polymer? Explain.

The PVC beads sink. The spacing between chains is similar, but a Cl atom has a greater mass than CH_3.	1 point is earned for the correct polymer with a correct explanation.

PP is synthesized from propene, C_3H_6, and PVC is synthesized from vinyl chloride, C_2H_3Cl. The structures of the molecules are shown below.



Propene



Vinyl Chloride (chloroethene)

(b) The boiling point of liquid propene (226 K) is lower than the boiling point of liquid vinyl chloride (260 K). Account for this difference in terms of the types and strengths of intermolecular forces present in each liquid.

Both substances have dipole-dipole interactions and London dispersion forces (or propene is essentially nonpolar with only LDFs while vinyl chloride has both LDFs and dipole-dipole forces). Propene contains a CH_3 group, but vinyl chloride contains a Cl atom. Vinyl chloride thus has a larger electron cloud, is more polarizable, and has a larger dipole moment. Thus intermolecular attractions are stronger in vinyl chloride, which results in it having the higher boiling point.	1 point is earned for a discussion of intermolecular forces and for a comparison of their relative strengths.

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2014 SCORING GUIDELINES

Question 6 (continued)

In a separate experiment, the student measures the enthalpies of combustion of propene and vinyl chloride. The student determines that the combustion of 2.00 mol of vinyl chloride releases 2300 kJ of energy, according to the equation below.

$$2\ C_2H_3Cl(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(g) + 2\ HCl(g) \qquad \Delta H^\circ = -2300\ \text{kJ/mol}_{rxn}$$

of propene releases more, less, or the same amount of energy that 2.00 mol of vinyl chloride releases. Justify your answer with a calculation. The balanced equation for the combustion of 2.00 mol of propene is $2\ C_3H_6(g) + 9\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g)$.

Substance	$C_2H_3Cl(g)$	$C_3H_6(g)$	$CO_2(g)$	$H_2O(g)$	$HCl(g)$	$O_2(g)$
Standard Enthalpy of Formation (kJ/mol)	37	21	−394	−242	−92	0

$\Delta H^\circ = 6(-394) + 6(-242) - 2(21) = -3858\ \text{kJ/mol}_{rxn}$ The combustion of 2.00 mol of propene releases more energy.	1 point is earned for the calculation of the enthalpy of combustion of propene. 1 point is earned for the comparison of propene to vinyl chloride that is consistent with the calculated value.

AP® CHEMISTRY
2009 SCORING GUIDELINES

Question 6 (8 points)

Answer the following questions related to sulfur and one of its compounds.

(a) Consider the two chemical species S and S^{2-}.

(i) Write the electron configuration (e.g., $1s^2\ 2s^2$ . . .) of each species.

S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ S^{2-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ Note: Replacement of $1s^2\ 2s^2\ 2p^6$ by [Ne] is acceptable.	One point is earned for the correct configuration for S. One point is earned for the correct configuration for S^{2-}.

(ii) Explain why the radius of the S^{2-} ion is larger than the radius of the S atom.

The nuclear charge is the same for both species, but the eight valence electrons in the sulfide ion experience a greater amount of electron-electron repulsion than do the six valence electrons in the neutral sulfur atom. This extra repulsion in the sulfide ion increases the average distance between the valence electrons, so the electron cloud around the sulfide ion has the greater radius.	One point is earned for a correct explanation.

(iii) Which of the two species would be attracted into a magnetic field? Explain.

The sulfur atom would be attracted into a magnetic field. Sulfur has two unpaired p electrons, which results in a net magnetic moment for the atom. This net magnetic moment would interact with an external magnetic field, causing a net attraction into the field. The sulfide ion would not be attracted into a magnetic field because all the electrons in the species are paired, meaning that their individual magnetic moments would cancel each other.	One point is earned for the correct answer with a correct explanation.

(b) The S^{2-} ion is isoelectronic with the Ar atom. From which species, S^{2-} or Ar, is it easier to remove an electron? Explain.

It requires less energy to remove an electron from a sulfide ion than from an argon atom. A valence electron in the sulfide ion is less attracted to the nucleus (charge +16) than is a valence electron in the argon atom (charge +18).	One point is earned for the correct answer with a correct explanation.

Question 6 (continued)

(c) In the H_2S molecule, the H–S–H bond angle is close to 90°. On the basis of this information, which atomic orbitals of the S atom are involved in bonding with the H atoms?

The atomic orbitals involved in bonding with the H atoms in H_2S are p (specifically, $3p$) orbitals. The three p orbitals are mutually perpendicular (i.e., at 90°) to one another.	One point is earned for the correct answer.

(d) Two types of intermolecular forces present in liquid H_2S are London (dispersion) forces and dipole-dipole forces.

(i) Compare the strength of the London (dispersion) forces in liquid H_2S to the strength of the London (dispersion) forces in liquid H_2O. Explain.

The strength of the London forces in liquid H_2S is greater than that of the London forces in liquid H_2O. The electron cloud of H_2S has more electrons and is thus more polarizable than the electron cloud of the H_2O molecule.	One point is earned for the correct answer with a correct explanation.

(ii) Compare the strength of the dipole-dipole forces in liquid H_2S to the strength of the dipole-dipole forces in liquid H_2O. Explain.

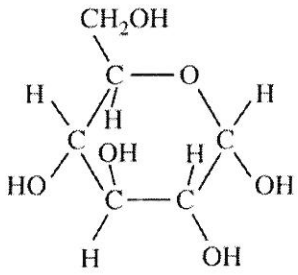
The strength of the dipole-dipole forces in liquid H_2S is weaker than that of the dipole-dipole forces in liquid H_2O. The net dipole moment of the H_2S molecule is less than that of the H_2O molecule. This results from the lesser polarity of the H–S bond compared with that of the H–O bond (S is less electronegative than O).	One point is earned for the correct answer with a correct explanation.

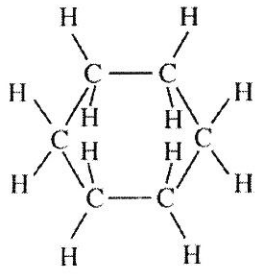
AP® CHEMISTRY
2006 SCORING GUIDELINES

Question 6

6. Answer each of the following in terms of principles of molecular behavior and chemical concepts.

(a) The structures for glucose, $C_6H_{12}O_6$, and cyclohexane, C_6H_{12}, are shown below.





Identify the type(s) of intermolecular attractive forces in

(i) pure glucose

Hydrogen bonding OR dipole-dipole interactions OR van der Waals interactions (London dispersion forces may also be mentioned.)	One point is earned for a correct answer.

(ii) pure cyclohexane

London dispersion forces	One point is earned for London dispersion forces.

(b) Glucose is soluble in water but cyclohexane is not soluble in water. Explain.

The hydroxyl groups in glucose molecules can form strong hydrogen bonds with the solvent (water) molecules, so glucose is soluble in water. In contrast, cyclohexane is not capable of forming strong intermolecular attractions with water (no hydrogen bonding), so the water-cyclohexane interactions are not as energetically favorable as the interactions that already exist among polar water molecules. **OR** • Glucose is polar and cyclohexane is nonpolar. • Polar solutes (such as glucose) are generally soluble in polar solvents such as water. • Nonpolar solutes (such as cyclohexane) are not soluble in the polar solvent.	One point is earned for explaining the solubility of glucose in terms of hydrogen bonding or dipole-dipole interactions with water. One point is earned for explaining the difference in the polarity of cyclohexane and water. **OR** One point is earned for any one of the three concepts; two points are earned for any two of the three concepts.

Question 6 (continued)

(c) Consider the two processes represented below.

Process 1: $H_2O(l) \rightarrow H_2O(g)$ $\quad \Delta H^\circ = +44.0 \text{ kJ mol}^{-1}$

Process 2: $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$ $\quad \Delta H^\circ = +286 \text{ kJ mol}^{-1}$

(i) For each of the two processes, identify the type(s) of intermolecular or intramolecular attractive forces that must be overcome for the process to occur.

In process 1, hydrogen bonds (or dipole-dipole interactions) in liquid water are overcome to produce distinct water molecules in the vapor phase.	One point is earned for identifying the type of intermolecular force involved in process 1.
In process 2, covalent bonds (or sigma bonds, or electron-pair bonds) within water molecules must be broken to allow the atoms to recombine into molecular hydrogen and oxygen.	One point is earned for identifying the type of intramolecular bonding involved in process 2.

(ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

When water boils, H_2O molecules break apart to form hydrogen molecules and oxygen molecules.

I disagree with the statement. Boiling is simply Process 1, in which only intermolecular forces are broken and the water molecules stay intact. No intramolecular or covalent bonds break in this process.	One point is earned for disagreeing with the statement and providing a correct explanation.

AP® CHEMISTRY
2015 SCORING GUIDELINES

Question 6

Compound	Melting Point (°C)
LiI	449
KI	686
LiF	845
NaF	993

A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

(a) Select two compounds from the table and explain how the data support the student's hypothesis.

LiI and KI. LiI has a small cation and a large anion and KI has a large cation and the same large anion. The melting point of LiI (with its smaller cation) is lower than that of KI. **OR** LiI and LiF. LiI has a small cation and a large anion and LiF has the same small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of LiF. **OR** LiI and NaF. LiI has a small cation and a large anion and NaF has a relatively small cation and a small anion. The melting point of LiI (with its larger anion) is lower than that of NaF.	1 point is earned for choosing an appropriate pair of compounds (LiI/KI, LiI/LiF, or LiI/NaF). 1 point is earned for an explanation that supports the hypothesis.

(b) Identify a compound from the table that can be dissolved in water to produce a basic solution. Write the net ionic equation for the reaction that occurs to cause the solution to be basic.

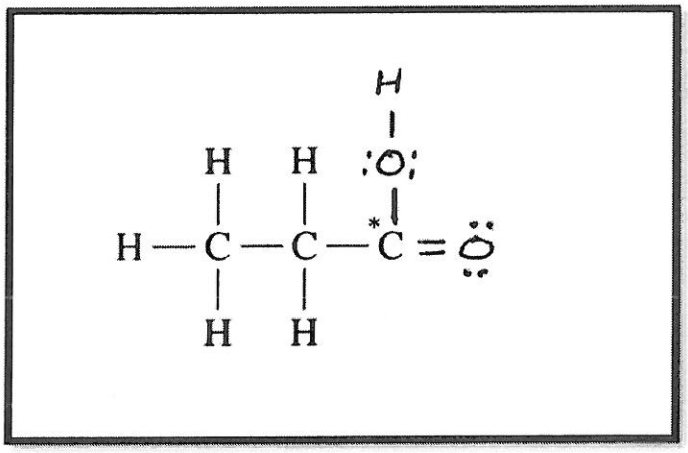
Either LiF or NaF is acceptable. $F^- + H_2O \rightleftarrows HF + OH^-$	1 point is earned for choosing one of the correct compounds. 1 point is earned for writing a correct balanced equation.

AP® CHEMISTRY
2016 SCORING GUIDELINES

Question 6

Propanoic acid, C_2H_5COOH, is an organic acid that is a liquid at room temperature.

(a) An incomplete Lewis diagram for the propanoic acid molecule is provided in the box below. Complete the diagram, showing how the remaining atoms in the molecule are arranged around the carbon atom marked with an asterisk (*). Your structure should minimize formal charge and include any lone pairs of electrons.



There should be two O atoms attached to the C atom, one with a double bond and one with a single bond. The O atom attached with a single bond should have an H atom attached to it. Each O atom has two lone pairs of electrons. (Figure is required.)	1 point is earned for a correct structure.

(b) Identify the hybridization of the carbon atom marked with the asterisk.

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

(c) Propanoic acid has a lower boiling point than butanoic acid, C_3H_7COOH.

(i) Identify all the types of intermolecular forces present among the molecules in propanoic acid.

London dispersion forces, dipole-dipole forces, and hydrogen bonding. (Identifying dipole-dipole forces is not required to earn the point.)	1 point is earned for identifying both London dispersion forces and hydrogen bonding.

(ii) Which of the types of intermolecular forces that you identified in part (c)(i) is most responsible for the difference in boiling points of the two acids?

London dispersion forces.	1 point is earned for the correct answer.

AP® CHEMISTRY
2016 SCORING GUIDELINES

Question 7

A student has 100. mL of 0.400 M $CuSO_4(aq)$ and is asked to make 100. mL of 0.150 M $CuSO_4(aq)$ for a spectrophotometry experiment. The following laboratory equipment is available for preparing the solution: centigram balance, weighing paper, funnel, 10 mL beaker, 150 mL beaker, 50 mL graduated cylinder, 100 mL volumetric flask, 50 mL buret, and distilled water.

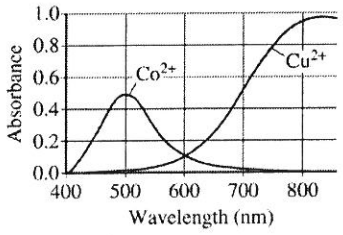
(a) Calculate the volume of 0.400 M $CuSO_4(aq)$ required for the preparation.

$M_1 V_1 = M_2 V_2$ $V_2 = \frac{(0.150\ M)(0.100\ \text{L})}{0.400\ M}$ $V_2 = 0.0375\ \text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 37.5\ \text{mL}$	1 point is earned for the correct volume.

(b) Briefly describe the essential steps to most accurately prepare the 0.150 M $CuSO_4(aq)$ from the 0.400 M $CuSO_4(aq)$ using the equipment listed above.

Use the buret to dispense 37.5 mL of $CuSO_4$ solution into the volumetric flask. Fill to the mark with distilled water.	1 point is earned for using the buret to measure 37.5 mL of 0.400 M $CuSO_4$ solution. 1 point is earned for adding the $CuSO_4$ solution to the volumetric flask and filling to the mark with distilled water.

The student plans to conduct a spectrophotometric analysis to determine the concentration of $Cu^{2+}(aq)$ in a solution. The solution has a small amount of $Co(NO_3)_2(aq)$ present as a contaminant. The student is given the diagram below, which shows the absorbance curves for aqueous solutions of $Co^{2+}(aq)$ and $Cu^{2+}(aq)$.



(c) The spectrophotometer available to the student has a wavelength range of 400 nm to 700 nm. What wavelength should the student use to minimize the interference from the presence of the $Co^{2+}(aq)$ ions?

700 nm (Any wavelength from 650 to 700 nm is acceptable.)	1 point is earned for a correct wavelength.

AP® CHEMISTRY
2012 SCORING GUIDELINES

Question 5
(8 points)

Process	$\Delta H°$ (kJ/mol$_{rxn}$)
$Br_2(l) \rightarrow Br_2(g)$	30.91
$I_2(s) \rightarrow I_2(g)$	62.44

At 298 K and 1 atm, the standard state of Br_2 is a liquid, whereas the standard state of I_2 is a solid. The enthalpy changes for the formation of $Br_2(g)$ and $I_2(g)$ from these elemental forms at 298 K and 1 atm are given in the table above.

(a) Explain why $\Delta H°$ for the formation of $I_2(g)$ from $I_2(s)$ is larger than $\Delta H°$ for the formation of $Br_2(g)$ from $Br_2(l)$. In your explanation identify the type of particle interactions involved and a reason for the difference in magnitude of those interactions.

Two reasons may be given. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar molecules, will be stronger in I_2 because of its greater number of electrons and larger size. The second reason is that since ΔH of sublimation is approximately ΔH of fusion plus ΔH of vaporization, $I_2(g)$ should have a larger $\Delta H°$ of formation since it involves sublimation, whereas $Br_2(g)$ formation involves only vaporization.	1 point is earned for identifying London dispersion forces. 1 point is earned for either of the following: explaining the reason for the greater LDFs in I_2 OR stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.

(b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.

$I_2(s) \rightarrow I_2(g)$ should have the greater change in entropy. The sublimation of I_2 may be thought of as a combination of fusion and vaporization. The conversion from solid to liquid would involve an increase in entropy, as would the conversion from liquid to gas. Br_2 is only undergoing the liquid to gas conversion and so will undergo a smaller entropy increase.	1 point is earned for the correct choice with a correct explanation.

Question 5 (continued)

(c) $I_2(s)$ and $Br_2(l)$ can react to form the compound $IBr(l)$. Predict which would have the greater molar enthalpy of vaporization, $IBr(l)$ or $Br_2(l)$. Justify your prediction.

$IBr(l)$. Two reasons may be given. First, IBr is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, IBr should have stronger London dispersion forces because of the greater number of electrons in the larger IBr molecule.	1 point is earned for the correct choice with either or both of the acceptable reasons.

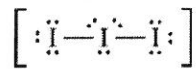
An experiment is performed to compare the solubilities of $I_2(s)$ in different solvents, water and hexane (C_6H_{14}). A student adds 2 mL of H_2O and 2 mL of C_6H_{14} to a test tube. Because H_2O and C_6H_{14} are immiscible, two layers are observed in the test tube. The student drops a small, purple crystal of $I_2(s)$ into the test tube, which is then corked and inverted several times. The C_6H_{14} layer becomes light purple, while the H_2O layer remains virtually colorless.

(d) Explain why the hexane layer is light purple while the water layer is virtually colorless. Your explanation should reference the relative strengths of interactions between molecules of I_2 and the solvents H_2O and C_6H_{14}, and the reasons for the differences.

The hexane layer is purple because most of the I_2 is dissolved in it. The entrance of the I_2 into water requires disruption of the hydrogen bonds in water, which are much stronger than the London dispersion forces in hexane. Meanwhile, the London dispersion forces between I_2 and hexane would be stronger than the London dispersion forces between I_2 and water. (Water and I_2 can also interact through a dipole-induced dipole force, but this attraction is insufficient to overcome the other differences noted above.)	1 point is earned for recognizing from the experimental observations that the iodine dissolved in the hexane. 1 point is earned for a correct explanation referencing the differences between water and hexane in their interactions with I_2.

(e) The student then adds a small crystal of $KI(s)$ to the test tube. The test tube is corked and inverted several times. The I^- ion reacts with I_2 to form the I_3^- ion, a linear species.

(i) In the box below, draw the complete Lewis electron-dot diagram for the I_3^- ion.

	1 point is earned for a correct Lewis diagram.

Question 5 (continued)

(ii) In which layer, water or hexane, would the concentration of I_3^- be higher? Explain.

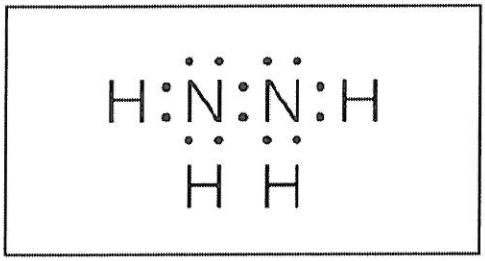
I_3^- would be more soluble in water because of the ion-dipole interactions that would occur between the ions and the polar water molecules. No such interactions are possible in the nonpolar hexane.	1 point is earned for the correct choice and explanation.

AP® CHEMISTRY
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.

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.

AP® CHEMISTRY
2013 SCORING GUIDELINES

Question 6
(9 points)

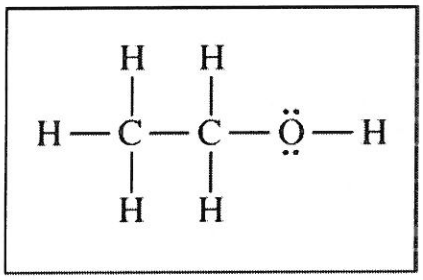
Answer the following questions using principles of molecular structure and intermolecular forces.

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.

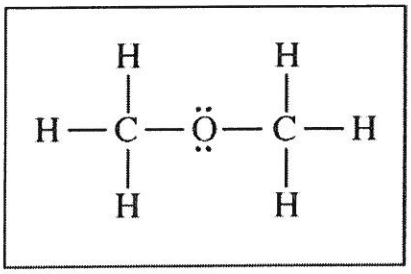
(i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.



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

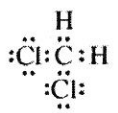
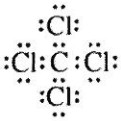
1 point is earned for a correct Lewis diagram.

Question 6 (continued)

(b) On the basis of the complete Lewis electron-dot diagrams you drew in part (a) and the information in the data table above, identify which compound, 1 or 2, has the structure represented in Box X. Justify your answer in terms of the intermolecular forces present in each compound.

Compound 2 is in Box X. Compound 2 (X) would have intermolecular hydrogen bonding. Compound 1 (Y) would have weaker dipole-dipole and London dispersion forces (LDFs). Because compound 2 has stronger intermolecular forces (IMFs) it has a higher boiling point. Also, compound 2 is capable of forming more hydrogen bonds with H_2O than compound 1 is, causing the solubility difference noted in the table.	2 points are earned for identification of compound 2 and a rationale that references the types of IMFs in each compound while explaining relative boiling points and/or solubilities.

Use the information in the following table to answer parts (c) and (d).

Name	Lewis Electron-Dot Diagram	Boiling Point (°C)	Vapor Pressure at 20°C (mm Hg)
Dichloromethane		39.6	353
Carbon tetrachloride		76.7	89

(c) Dichloromethane has a greater solubility in water than carbon tetrachloride has. Account for this observation in terms of the intermolecular forces between <u>each</u> of the solutes and water.

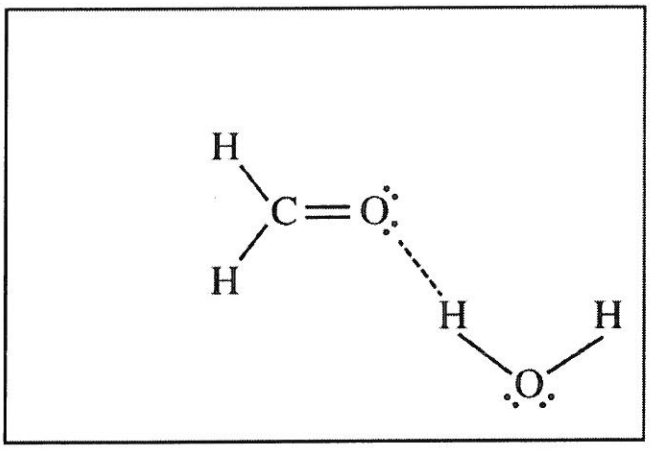
CH_2Cl_2 is polar, whereas CCl_4 is not. Therefore, CH_2Cl_2 interacts with H_2O via dipole-dipole forces, while CCl_4 only interacts with water via dipole/induced dipole forces or LDFs, which would be weaker. As a result, CH_2Cl_2 has a greater solubility.	2 points are earned for a rationale that references the types of IMFs between each compound and water.

(d) In terms of intermolecular forces, explain why dichloromethane has a higher vapor pressure than carbon tetrachloride.

Because CH_2Cl_2 has the higher vapor pressure, the combination of LDFs and dipole-dipole forces in CH_2Cl_2 must be weaker than the strong LDFs in CCl_4.	2 points are earned (1 point for referencing the type(s) of IMFs in <u>each</u> of the two compounds).

Question 6 (continued)

(e) The complete Lewis electron dot diagram of methanal (formaldehyde) is shown in the box below. Molecules of methanal can form hydrogen bonds with water. In the box below, draw a water molecule in a correct orientation to illustrate a hydrogen bond between a molecule of water and the molecule of methanal. Use a dashed line to represent the hydrogen bond.



See diagram above.	1 point is earned for a correct diagram.

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2016 SCORING GUIDELINES

Question 4

Element	Atomic Radius (pm)
Au	135
Pd	140

White gold is a common alloy of gold and palladium that is often used in jewelry. The atomic radii of the metals are given in the table above.

(a) A particular ring is made from an alloy that is 75 mole percent gold and 25 mole percent palladium. Using the box below, draw a particle-level diagram of the solid alloy consisting of 12 atoms with a representative proportion of atom types. Your diagram should clearly indicate whether the alloy is interstitial or substitutional. Use empty circles for gold and shaded circles for palladium.

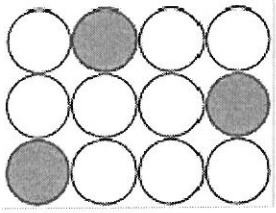

Diagram should show 12 circles in a regular array, 9 empty and 3 shaded.	1 point is earned for the correct number of each type of circle. 1 point is earned for showing an acceptable arrangement (i.e., regular array of circles of about the same size).

White-gold jewelry is often coated with rhodium to modify the color and durability.

(b) A student hypothesizes that placing the ring in a 1.0 M solution of $Rh(NO_3)_3(aq)$ will result in a reaction in which Rh metal is deposited on the white-gold ring. Based on the information in the table below, calculate $E°$ for the reactions that may occur between ions in the solution and atoms in the ring, and indicate whether or not the student's hypothesis is correct.

Half-Reaction	$E°$ (V)
$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$	1.50
$Pd^{2+}(aq) + 2\ e^- \rightarrow Pd(s)$	0.92
$Rh^{3+}(aq) + 3\ e^- \rightarrow Rh(s)$	0.76

$Au + Rh^{3+} \rightarrow Au^{3+} + Rh$ $0.76\ V - 1.50\ V = -0.74\ V$ $3\ Pd + 2\ Rh^{3+} \rightarrow 3\ Pd^{2+} + 2\ Rh$ $0.76\ V - 0.92\ V = -0.16\ V$	1 point is earned for the $E°$ calculations.
The student's hypothesis is incorrect. (Both voltages are negative, so the reactions are not thermodynamically favorable under these conditions.)	1 point is earned for the claim.

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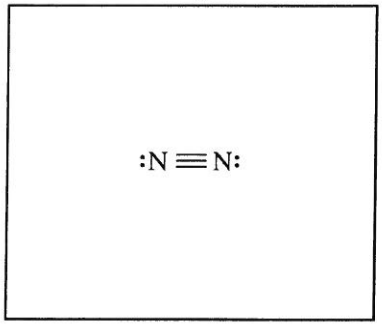
2009 SCORING GUIDELINES (Form B)

Question 5 (9 points)

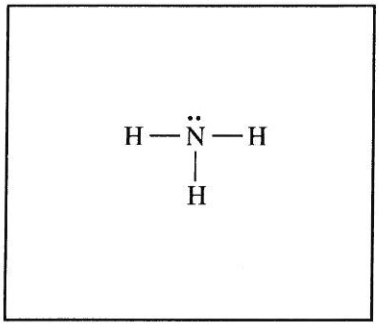
Answer the following questions about nitrogen, hydrogen, and ammonia.

(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.

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

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

(c) Given that ΔH°_{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.

$\Delta H^\circ_{298} = \Sigma$ (bond energy of the reactants) $- \Sigma$ (bond energy of the products) Based on the equation above, for ΔH°_{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 $\Delta H°$ and $\Delta S°$ 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 $\Delta G°$ changes.

$\Delta G° = \Delta H° - T\Delta S°$ As the temperature increases $\lvert T\Delta S°\rvert$ will at some point exceed $\lvert\Delta H°\rvert$. Because both $\Delta H°$ and $\Delta S°$ are negative, the sign of $\Delta G°$ 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.

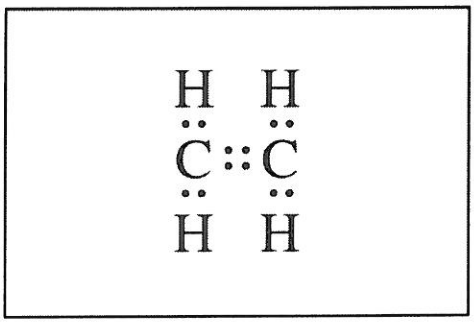
Question 2 (continued)

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

(c) Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of ΔG°_{298} for the reaction.

Yes, the data support the student's claim. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= 45.5\ \text{kJ/mol}_{rxn} - (298\ \text{K})(0.126\ \text{kJ/(K·mol}_{rxn}\text{))} = 8.0\ \text{kJ/mol}_{rxn}$ Because $\Delta G^\circ > 0$, the value of $K_p = e^{\left(\frac{-\Delta G^\circ}{RT}\right)} < 1.00$.	1 point is earned for the correct calculation of ΔG°. 1 point is earned for a valid justification.

(d) The Lewis electron-dot diagram for C_2H_4 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for C_2H_5OH by drawing in all of the electron pairs.



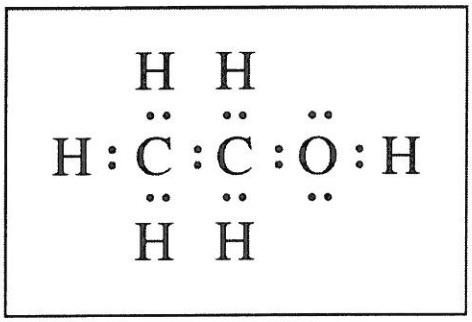


Diagram should include all bonding pairs plus two nonbonding pairs on the O atom. (A line may be used to represent an electron pair.)	1 point is earned for a correct diagram.

(e) What is the approximate value of the C–O–H bond angle in the ethanol molecule?

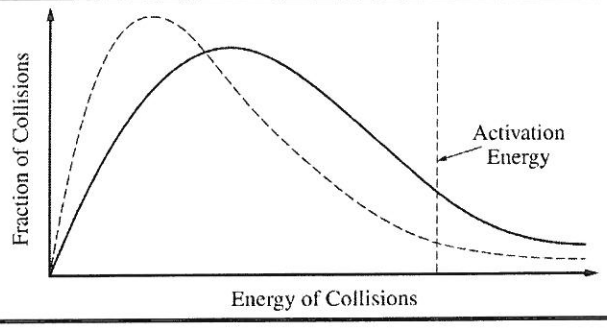
The bond angle is approximately 109°.	1 point is earned for an angle from 100° to 115°.

Question 2 (continued)

(f) During the dehydration experiment, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

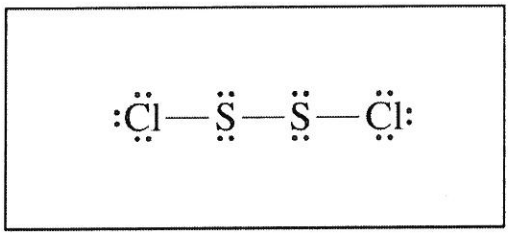
Ethene is only slightly soluble in water because the weak dipole/induced dipole intermolecular attractions between nonpolar ethene molecules and polar water molecules are weaker than the hydrogen bonds between water molecules. Ethanol molecules are soluble in water because they are polar and form hydrogen bonds with water molecules as they dissolve.	1 point is earned for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of differences in polarity. 1 point is earned for describing the intermolecular forces between ethene and water as weak dipole/induced dipole forces and attributing the solubility of ethanol in water to the hydrogen bonds formed between ethanol molecules and water molecules.

Question 1 (continued)

	1 point is earned for a curve that has a peak above and to the left of the given curve. 1 point is earned for a curve that is below the given curve in the region beyond the activation energy.

(c) S_2Cl_2 is a product of the reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.



See correct diagram above.	1 point is earned for a correctly drawn diagram.

(ii) What is the approximate value of the Cl–S–S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl–S–S bond angles are not equal, include both angles.)

Any value between 104° and 110°	1 point is earned for an acceptable angle that is consistent with the Lewis diagram.

(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

Question 1 (continued)

(i) Identify all types of intermolecular forces present in $HCl(l)$.

Dipole-dipole forces, London dispersion forces	1 point is earned for both types of forces.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

The intermolecular forces among CCl_4 molecules must be **stronger** than those among HCl molecules because the CCl_4 condenses at a higher temperature than HCl.	1 point is earned for the correct answer with a valid justification.

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Question 6
(8 points)

6. Answer the following questions relating to the elements gallium and arsenic.

(a) Write the ground-state electron configuration for an atom of each of the following.

(i) Ga

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or $[Ar]4s^2 3d^{10} 4p^1$	One point is earned for correct configuration.

(ii) As

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ or $[Ar]4s^2 3d^{10} 4p^3$	One point is earned for correct configuration.

(b) Consider the information in the table below

	First Ionization Energy ($kJ\ mol^{-1}$)	Second Ionization Energy ($kJ\ mol^{-1}$)
Gallium	580	1,980
Arsenic	950	1,800

(i) Explain, in terms of atomic structure, why As has a higher first ionization energy than Ga.

The electron ionized from As experiences a higher nuclear charge than the electron ionized from Ga, simply because the As nucleus has two more protons than the Ga nucleus.	One point is earned for the correct explanation.

(ii) Explain, in terms of atomic structure, why Ga has a higher second ionization energy than As.

The second electron removed from Ga comes from the 4s subshell which is lower in energy compared to the second electron removed from As, which comes from the 4p subshell.	One point is earned for the correct explanation.

Question 6 (continued)

(d) Consider the Ga^+ ion.

(i) Identify an ion of As that is isoelectronic with Ga^+.

As^{3+}	One point is earned for correct identification of the ion.

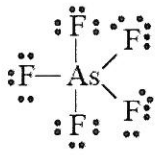
(ii) Which species has a larger radius: Ga^+ or the ion you identified in part (c)(i) ? Explain.

Ga^+ would be larger; the outer electrons in the Ga^+ ion are held less tightly because the Ga nucleus has fewer protons than the As nucleus. The result is a larger ion.	One point is earned for the correct choice with a correct explanation.

Must be consistent with the response in (c)(i).

(d) Arsenic reacts with fluorine to form AsF_5 .

(i) Draw the complete Lewis electron-dot diagram for the AsF_5 molecule.

	One point is earned for the correct Lewis structure.

(ii) Are all of the F–As–F bond angles in the AsF_5 molecule the same? Explain.

No; the structure is trigonal bipyramidal, so the angle between the axial F and the equatorial F is 90° while the angle between the equatorial F's is 120°. The angle between axial F's is 180°	One point is earned for the correct response with explanation.

Consistent with the structure in d(i). For example, trigonal bipyramidal and consists of two different angles, or a difference in angles.

Question 7

Use principles of atomic structure, bonding, and/or intermolecular forces to respond to each of the following. Your responses must include specific information about all substances referred to in each question.

(a) At a pressure of 1 atm, the boiling point of $NH_3(l)$ is 240 K, whereas the boiling point of $NF_3(l)$ is 144 K.

(i) Identify the intermolecular forces(s) in each substance.

NH_3 has dispersion forces and hydrogen-bonding forces. NF_3 has dispersion forces and dipole-dipole forces. (Credit earned for hydrogen-bonding and dipole-dipole forces)	One point is earned for the correct intermolecular attractive forces for both NH_3 and NF_3.

(ii) Account for the difference in the boiling points of the substances.

The higher boiling point for NH_3 is due to the greater strength of the hydrogen-bonding intermolecular attractive forces among NH_3 molecules compared to that of the dipole-dipole attractive forces among NF_3 molecules.	One point is earned for correctly identifying NH_3 as having stronger intermolecular forces than NF_3.

(b) The melting point of $KCl(s)$ is 776°C, whereas the melting point of $NaCl(s)$ is 801°C.

(i) Identify the type of bonding in each substance.

Both KCl and NaCl have ionic bonds.	One point is earned for naming ionic bonds as the bonds in KCl and NaCl.

(ii) Account for the difference in the melting points of the substances.

The difference in the melting points is due to the different strengths of ionic bonding in the substances. The charges on the cations and anions are the same in both compounds, therefore the relative size of the ions is the determining factor. Since Na^+ has a smaller ionic radius than K^+, the lattice energy of NaCl is higher than that of KCl. Thus more energy is required to overcome the ionic forces in solid NaCl than in solid KCl, and NaCl has the higher melting point.	One point is earned for a correct explanation of the cause of the difference in melting points of KCl and NaCl.

Question 7 (continued)

(c) As shown in the table below, the first ionization energies of Si , P, and Cl show a trend.

Element	First Ionization Energy ($kJ\ mol^{-1}$)
Si	786
P	1,012
Cl	1,251

(i) For each of the three elements, identify the quantum level (e.g., $n = 1$, $n = 2$, etc.) of the valence electrons in the atom.

The valence electron is located in the $n = 3$ level for all three atoms.	One point is earned for the principal quantum level for all three elements.

(ii) Explain the reasons for the trend in first ionization energies.

Because the valence electrons in all three elements are shielded by the same number of inner core electrons and the nuclear charge increases going from Si to P to Cl, the valence electrons feel an increasing attraction to the nucleus going from Si to P to Cl. Valence electrons having a greater attraction to the nucleus, as in Cl , will be more difficult to remove, so Cl has the highest ionization energy. P has the second highest ionization energy, and Si has the lowest ionization energy.	One point is earned for explaining that greater ionization energy is due to increased nuclear charge. Note: Explanations of the trend on the basis of effective nuclear charge are acceptable.

(d) A certain element has two stable isotopes. The mass of one of the isotopes is 62.93 amu and the mass of the other isotope is 64.93 amu.

(i) Identify the element. Justify your answer.

Copper. The relative average atomic mass is between the two isotopic masses given.	One point is earned for the element and the explanation.

(ii) Which isotope is more abundant? Justify your answer.

The isotope with mass 62.93 amu must be more abundant because its mass is closer to 63.55 amu (the relative weighted average atomic mass for copper) than is the mass of the other isotope.	One point is earned for the correct choice and explanation.