AP

AP® Chemistry
2013 Scoring Guidelines

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CollegeBoard

Answer the following questions about the solubility of some fluoride salts of alkaline earth metals.

(a) A student prepares 100. mL of a saturated solution of MgF_2 by adding 0.50 g of solid MgF_2 to 100. mL of distilled water at 25°C and stirring until no more solid dissolves. (Assume that the volume of the undissolved MgF_2 is negligibly small.) The saturated solution is analyzed, and it is determined that $[F^-]$ in the solution is $2.4 \times 10^{-3}\ M$.

   (i)   Write the chemical equation for the dissolving of solid MgF_2 in water.

$MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ F^-(aq)$	1 point is earned for the correct equation.

   (ii) Calculate the number of moles of MgF_2 that dissolved.

$\dfrac{2.4 \times 10^{-3}\,\text{mol F}^-}{1.0\ \text{L}} \times 0.100\ \text{L} \times \dfrac{1\ \text{mol MgF}_2}{2\ \text{mol F}^-} = 1.2 \times 10^{-4}\ \text{mol MgF}_2$	1 point is earned for the correct calculation of moles from concentration. 1 point is earned for the correct stoichiometry.

   (iii) Determine the value of the solubility-product constant, K_{sp}, for MgF_2 at 25°C.

$[Mg^{2+}] = \dfrac{1}{2}\,[F^-] = \dfrac{1}{2}\,(2.4 \times 10^{-3}\ M) = 1.2 \times 10^{-3}\ M$ $K_{sp} = [Mg^{2+}][F^-]^2 = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2$ $\quad = 6.9 \times 10^{-9}$	1 point is earned for the correct value of $[Mg^{2+}]$ 1 point is earned for the correct setup for determining the value of K_{sp}. 1 point is earned for the correct value of K_{sp}.

(b) A beaker contains 500. mL of a solution in which both $Ca^{2+}(aq)$ and $Ba^{2+}(aq)$ are present at a concentration of 0.10 M at 25°C. A student intends to separate the ions by adding 0.20 M NaF solution one drop at a time from a buret. At 25°C the value of K_{sp} for CaF_2 is 3.5×10^{-11}; the value of K_{sp} for BaF_2 is 1.8×10^{-6}.

    (i) Which salt will precipitate first, CaF_2 or BaF_2 ? Justify your answer.

CaF_2 will precipitate first. Its K_{sp} value is smaller, thus the ion-concentration product $[Ca^{2+}][F^-]^2$ will be the first to exceed the K_{sp} value.	1 point is earned for the correct choice with its justification.

For parts (b)(ii) and (b)(iii) below, assume that the addition of the NaF solution does not significantly affect the total volume of the liquid in the beaker.

    (ii) Calculate the minimum concentration of $F^-(aq)$ necessary to initiate precipitation of the salt selected in part (b)(i).

$K_{sp} = 3.5 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (0.10)[F^-]^2$ $3.5 \times 10^{-10} = [F^-]^2$ $[F^-] = \sqrt{3.5 \times 10^{-10}} = 1.9 \times 10^{-5} M$	1 point is earned for the correct value of $[F^-]$.

    (iii) Calculate the minimum volume of 0.20 M NaF that must be added to the beaker to initiate precipitation of the salt selected in part (b)(i).

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Assuming that the volume of added NaF(aq) is negligible, the total volume of the solution at the point of precipitation is 500. mL. $(0.20 M)(V) = (1.9 \times 10^{-5} M)(0.500 L)$ $V = 4.7 \times 10^{-5} L$ (or $4.8 \times 10^{-5} L$) $= 4.7 \times 10^{-2}$ mL (or 4.8×10^{-2} mL)	1 point is earned for the correct volume.

(c) There are several ways to dissolve salts that have limited solubility. Describe one procedure to redissolve the precipitate formed in part (b).

Valid procedures include adding water, adding acid (H^+), heating (i.e., increasing the temperature), and any valid statement that implies a shifting of the equilibrium toward the products side of the dissolution equation.	1 point is earned for a description of a valid procedure.

Question 2

Answer the following questions involving the stoichiometry and thermodynamics of reactions containing aluminum species.

$$2 \text{ Al}_2\text{O}_3(l) + 3 \text{ C}(s) \rightarrow 4 \text{ Al}(l) + 3 \text{ CO}_2(g)$$
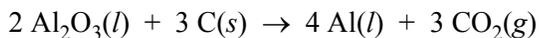
An electrolytic cell produces 235 g of $\text{Al}(l)$ according to the equation above.

(a) Calculate the number of moles of electrons that must be transferred in the cell to produce the 235 g of $\text{Al}(l)$.

$235 \text{ g Al} \times \dfrac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 8.71 \text{ mol Al}$ $\text{Al}^{3+} + 3 \, e^- \rightarrow \text{Al}$, therefore, 3 mol e^- transferred per mol Al $8.71 \text{ mol Al} \times \dfrac{3 \text{ mol } e^-}{1 \text{ mol Al}} = 26.1 \text{ mol } e^-$	1 point is earned for the number of moles of Al. 1 point is earned for correct stoichiometry and the number of moles of electrons.

(b) A steady current of 152 amp was used during the process. Determine the amount of time, in seconds, that was needed to produce the $\text{Al}(l)$.

$\text{charge} = \text{moles } e^- \times \text{Faraday's constant}$ $\qquad = 26.1 \text{ mol } e^- \times \dfrac{9.65 \times 10^4 \text{ C}}{1 \text{ mol } e^-} = 2.52 \times 10^6 \text{ C}$ $I = \dfrac{q}{t}$ $t = \dfrac{q}{I} = \dfrac{2.52 \times 10^6 \text{ C}}{152 \text{ C/s}} = 1.66 \times 10^4 \text{ s}$	1 point is earned for the correct amount of charge transferred. 1 point is earned for the correct time.

(c) Calculate the volume of $\text{CO}_2(g)$, measured at 301 K and 0.952 atm, that is produced in the process.

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$\text{mol CO}_2 = 8.71 \text{ mol Al} \times \dfrac{3 \text{ mol CO}_2}{4 \text{ mol Al}} = 6.53 \text{ mol CO}_2$ $PV = nRT$ $V = \dfrac{nRT}{P} = \dfrac{(6.53 \text{ mol})\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(301 \text{ K})}{0.952 \text{ atm}} = 1.70 \times 10^2 \text{ L CO}_2$	1 point is earned for the number of moles of CO_2. 1 point is earned for the volume of CO_2.

(d) For the electrolytic cell to operate, the Al_2O_3 must be in the liquid state rather than in the solid state. Explain.

Al_2O_3 is an ionic compound; in the solid state it will not conduct electricity. In order for the cell to operate, Al_2O_3 must be in the liquid state so that the ions are mobile and able to move to the electrodes to react (and/or complete the circuit).	1 point is earned for a correct explanation.

When Al(s) is placed in a concentrated solution of KOH at 25°C, the reaction represented below occurs.

$$2\,Al(s) + 2\,OH^-(aq) + 6\,H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3\,H_2(g)$$
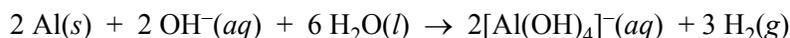
Half-reaction	$E°$ (V)
$[Al(OH)_4]^-(aq) + 3\,e^- \rightarrow Al(s) + 4\,OH^-(aq)$	−2.35
$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$	−0.83

(e) Using the table of standard reduction potentials shown above, calculate the following.

(i) $E°$, in volts, for the formation of $[Al(OH)_4]^-(aq)$ and $H_2(g)$ at 25°C

$E° = E°_{cathode} - E°_{anode} = -0.83\,\text{V} - (-2.35\,\text{V}) = 1.52\,\text{V}$	1 point is earned for the correct value of $E°$.

(ii) $\Delta G°$, in kJ/mol$_{rxn}$, for the formation of $[Al(OH)_4]^-(aq)$ and $H_2(g)$ at 25°C

$\Delta G° = -nFE° = -(6)(9.65 \times 10^4\,\text{C})(1.52\,\text{V})$ $= -8.80 \times 10^5\,\text{J/mol}_{rxn} = -8.80 \times 10^2\,\text{kJ/mol}_{rxn}$ (or $-880.\,\text{kJ/mol}_{rxn}$)	1 point is earned for $n = 6$. 1 point is earned for the correct value of $\Delta G°$.

Question 3
(9 points)

$$MgO(s) \ + \ 2 \ H^+(aq) \ \rightarrow \ Mg^{2+}(aq) \ + \ H_2O(l)$$
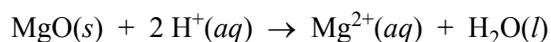
A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
3	100.0	0.25	26.0	28.1
4	100.0	0.50	24.1	28.1

(a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.

$0.100 \ \text{L} \times \dfrac{1.0 \ \text{mol HCl}}{1.0 \ \text{L}} = 0.10 \ \text{mol HCl}$ $0.50 \ \text{g MgO} \times \dfrac{1 \ \text{mol MgO}}{40.30 \ \text{g MgO}} = 0.0124 \ \text{mol MgO}$ By the stoichiometry of the equation, only $2 \times (0.0124 \ \text{mol}) = 0.025 \ \text{mol HCl}$ is needed to react with the MgO, thus HCl is in excess and MgO is limiting. OR The temperature change depended on the amount of MgO added, indicating that MgO was the limiting reactant.	1 point is earned for the correct choice with justification.

(b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

Trial 1 is inconsistent. The temperature change should be directly proportional (approximately) to the amount of the limiting reactant present. The ratio $\Delta T /(\text{mass MgO})$ should be constant. In trial 1, the ratio is one-half of trials 2, 3, and 4. Therefore, trial 1 is inconsistent with the other trials.	1 point is earned for identifying trial 1 with a valid justification.

For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is 4.18 J/(g·C°). Assume that the density of the HCl(aq) is 1.0 g/mL.

(c) Calculate the magnitude of q, the thermal energy change, when the MgO was added to the 1.0 M HCl(aq). Include units with your answer.

$q_{calorimeter} = q_{cal} = mc\Delta T$ In trial 2, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.50 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot {}^{\circ}\text{C}}\right)\left(4.1\,{}^{\circ}\text{C}\right) = 1700 \text{ J or } 1.7 \text{ kJ}$ OR In trial 3, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.25 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot {}^{\circ}\text{C}}\right)\left(2.1\,{}^{\circ}\text{C}\right) = 880 \text{ J or } 0.88 \text{ kJ}$ OR In trial 4, $q_{cal} = \left[\left(100.0 \text{ mL} \times \dfrac{1.0 \text{ g}}{\text{mL}}\right) + 0.50 \text{ g}\right]\left(\dfrac{4.18 \text{ J}}{\text{g} \cdot {}^{\circ}\text{C}}\right)\left(4.0\,{}^{\circ}\text{C}\right) = 1700 \text{ J or } 1.7 \text{ kJ}$	1 point is earned for the correct mass of the solution. 1 point is earned for the correct calculation of q for any trial with a valid ΔT and correct units.

(d) Determine the student's experimental value of $\Delta H°$ for the reaction between MgO and HCl in units of kJ/mol$_{rxn}$.

Assuming that no heat was lost to the surroundings, $q_{rxn} = -q_{cal}$. In trials 2 and 4, $\Delta H° = \dfrac{q_{rxn}}{n_{\text{MgO}}} = \dfrac{-1,700 \text{ J}}{0.50 \text{ g MgO} \times \dfrac{1 \text{ mol MgO}}{40.30 \text{ g MgO}}} = -140,000 \text{ J/mol}_{rxn} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}}$ $= -140 \text{ kJ/mol}_{rxn}$ In trial 3, $\Delta H° = \dfrac{-880 \text{ J}}{0.25 \text{ g MgO} \times \dfrac{1 \text{ mol MgO}}{40.30 \text{ g MgO}}} = -140,000 \text{ J/mol}_{rxn} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}}$ $= -140 \text{ kJ/mol}_{rxn}$	1 point is earned for the correct calculation of moles of MgO or setup of equation. 1 point is earned for the value of $\Delta H°$ and sign consistent with the setup.

(e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of $\Delta H°$ for the reaction between MgO(s) and HCl(aq).

Substance	$\Delta H_f°$ (kJ/mol)
MgO(s)	−602
$H_2O(l)$	−286
$H^+(aq)$	0
$Mg^{2+}(aq)$	−467

$$\Delta H° = \sum n_p \Delta H_f° \text{ products} - \sum n_r \Delta H_f° \text{ reactants}$$

$$= \left[\Delta H_f° \, Mg^{2+}(aq) + \Delta H_f° \, H_2O(l) \right] - \left[\Delta H_f° \, MgO(s) + 2 \, \Delta H_f° \, H^+(aq) \right]$$

$$= \left[-467 \text{ kJ/mol} + (-286 \text{ kJ/mol}) \right] - \left[-602 \text{ kJ/mol} + 2(0) \text{ kJ/mol} \right]$$

$$= -151 \text{ kJ/mol}_{rxn}$$

1 point is earned for the correct setup using the $\Delta H_f°$ values.

1 point is earned for the correct value and sign consistent with the setup.

(f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

Yes. The experimentally determined value for $\Delta H°$ was less negative than the accepted value. If heat had leaked out of the calorimeter, then the ΔT of the contents would be less than expected, leading to a smaller calculated value for q and a less negative value for $\Delta H°$.

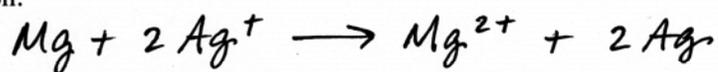1 point is earned for the correct response with a valid explanation.

Question 4
(15 points)

For each of the following three reactions, write a balanced equation for the reaction in part (i) and answer the question about the reaction in part (ii). In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be scored.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:

$$Mg + 2 Ag^+ \longrightarrow Mg^{2+} + 2 Ag$$

(ii) Which substance is oxidized in the reaction?

Mg is oxidized.

(a) A 20.0 mL sample of 0.10 M potassium phosphate is added to a 30.0 mL sample of 0.10 M calcium chloride.

(i) $3 Ca^{2+} + 2 PO_4^{3-} \rightarrow Ca_3(PO_4)_2$	2 points are earned for the correct reactants. 1 point is earned for the correct product. 1 point is earned for the correct balance of both mass and charge.

(ii) How many moles of product are formed?

$V \times M = (0.0200 \text{ L})(0.10 \text{ } M) = 0.0020 \text{ mol } PO_4^{3-}$ $V \times M = (0.0300 \text{ L})(0.10 \text{ } M) = 0.0030 \text{ mol } Ca^{2+}$ Therefore, 0.0010 mole of $Ca_3(PO_4)_2$ is formed.	1 point is earned for the correct number of moles with mathematical justification.

(b) Carbon dioxide gas is bubbled into freshly distilled water.

(i) $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$ OR $CO_2 + 2 H_2O \rightarrow H_3O^+ + HCO_3^-$ OR $CO_2 + H_2O \rightarrow H_2CO_3$	1 point is earned for the correct reactants. 2 points are earned for the correct product(s). 1 point is earned for the correct balance of both mass and charge.

   (ii)   The pH of the solution decreases as the reaction proceeds. Explain.

The reaction produces an acidic species. The solution pH decreases as $[H^+]$ increases.	1 point is earned for a correct explanation.

(c) A piece of zinc metal is placed in a 1.0 M solution of hydrochloric acid at 25°C.

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(i) $Zn + 2 H^+ \rightarrow Zn^{2+} + H_2$	1 point is earned for the correct reactants. 2 points are earned for the correct products. 1 point is earned for the correct balance of both mass and charge.

   (ii)   When a piece of zinc metal is placed in a 1.0 M solution of ethanoic (acetic) acid at 25°C, the rate of reaction is slower than when 1.0 M hydrochloric acid at 25°C is used. Explain.

Ethanoic acid is a weak acid while HCl is a strong acid, so $[H^+]$ will be less than it would be with HCl. The rate of reaction depends on $[H^+]$, so the rate will be slower in ethanoic acid than in hydrochloric acid.	1 point is earned for a correct explanation.

Question 5
(8 points)

A sample of $C_2H_4(g)$ is placed in a previously evacuated, rigid 2.0 L container and heated from 300 K to 450 K. The pressure of the sample is measured and plotted in the graph below.
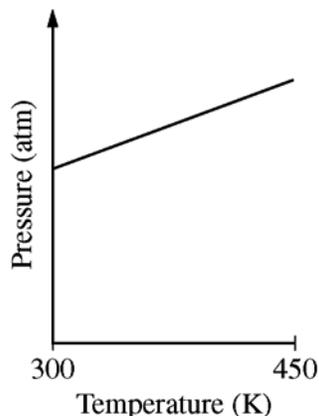
(a) Describe TWO reasons why the pressure changes as the temperature of the $C_2H_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

Two reasons are: (1) As the temperature increases, the average speed of the molecules increases and the molecules collide more frequently with the container walls. (2) As the temperature increases, the average kinetic energy of the molecules increases and the molecules strike the walls of the container with greater force.	1 point is earned for <u>each</u> correct reason.

$C_2H_4(g)$ reacts readily with $HCl(g)$ to produce $C_2H_5Cl(g)$, as represented by the following equation.

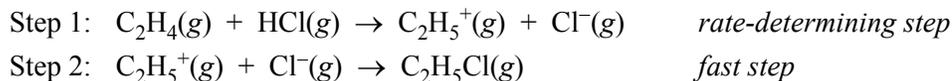$$C_2H_4(g) \ + \ HCl(g) \ \rightarrow \ C_2H_5Cl(g) \qquad \Delta H° = -72.6 \text{ kJ/mol}_{rxn}$$

(b) When $HCl(g)$ is injected into the container of $C_2H_4(g)$ at 450 K, the total pressure increases. Then, as the reaction proceeds at 450 K, the total pressure decreases. Explain this decrease in total pressure in terms of what occurs at the molecular level.

The decrease in pressure after the initial increase is a consequence of the reaction that produces fewer gas molecules than it consumes. When fewer gas molecules are present, there are fewer collisions with the container walls, resulting in a decrease in pressure.	1 point is earned for the correct reason.

It is proposed that the formation of $C_2H_5Cl(g)$ proceeds via the following two-step reaction mechanism.

Step 1: $C_2H_4(g) + HCl(g) \rightarrow C_2H_5^+(g) + Cl^-(g)$ *rate-determining step*

Step 2: $C_2H_5^+(g) + Cl^-(g) \rightarrow C_2H_5Cl(g)$ *fast step*

(c) Write the rate law for the reaction that is consistent with the reaction mechanism above.

$rate = k[C_2H_4][HCl]$	1 point is earned for the correct rate law.

(d) Identify an intermediate in the reaction mechanism above.

$C_2H_5^+(g)$ or $Cl^-(g)$	1 point is earned for identification of either species.

(e) Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two-step mechanism and the enthalpy change of the reaction.
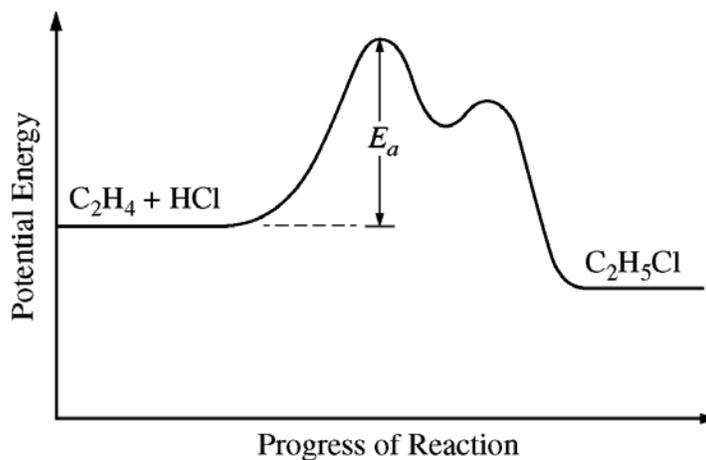
See drawing above.	1 point is earned for the potential energy of the product being lower than the potential energy of the reactants (exothermic reaction). 1 point is earned for a reaction-energy curve that reflects a two-step process.

(f) On the diagram above, clearly indicate the activation energy, E_a, for the rate-determining step in the reaction.

| *See drawing above in part (e).*	1 point is earned for the correct identification of E_a in Step 1.

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.
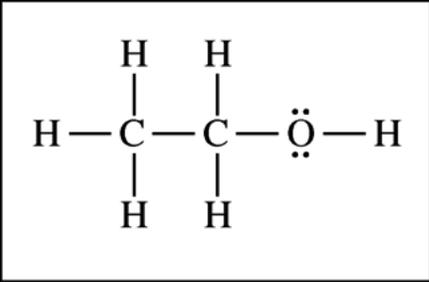
 Box X	1 point is earned for a correct Lewis diagram.

   (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.
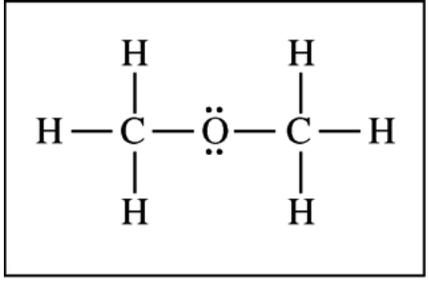
 Box Y	1 point is earned for a correct Lewis diagram.

(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	$\overset{\displaystyle H}{\underset{\displaystyle :\ddot{C}l:}{:\ddot{C}l:C:H}}$	39.6	353
Carbon tetrachloride	$\overset{\displaystyle :\ddot{C}l:}{\underset{\displaystyle :\ddot{C}l:}{:\ddot{C}l:C:\ddot{C}l:}}$	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 _each_ of the solutes and water.

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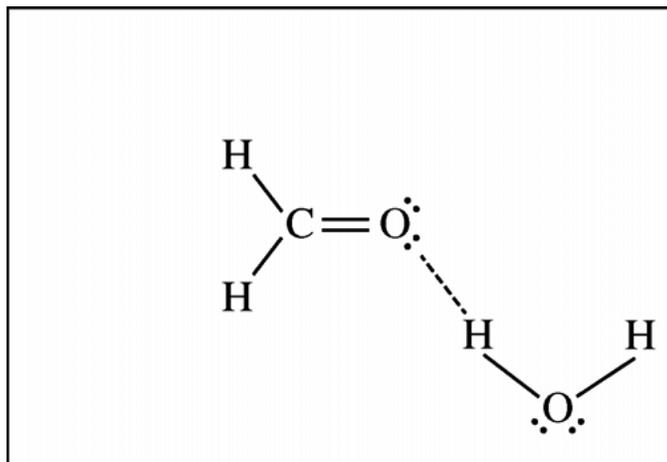
See diagram above.	1 point is earned for a correct diagram.