AP® Chemistry
2011 Scoring Guidelines
Form B

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Question 1
(10 points)

Answer the following questions about the solubility and reactions of the ionic compounds $M(OH)_2$ and MCO_3, where M represents an unidentified metal.

(a) Identify the charge of the M ion in the ionic compounds above.

2+	1 point is earned for the correct charge.

(b) At 25°C, a saturated solution of $M(OH)_2$ has a pH of 9.15.

(i) Calculate the molar concentration of $OH^-(aq)$ in the saturated solution.

pOH = 14 – pH pOH = 14 – 9.15 = 4.85 $[OH^-] = 10^{-4.85} = 1.4 \times 10^{-5}\ M$	1 point is earned for the correct concentration.

(ii) Write the solubility-product constant expression for $M(OH)_2$.

$K_{sp} = [M^{2+}]\,[OH^-]^2$	1 point is earned for the correct expression.

(iii) Calculate the value of the solubility-product constant, K_{sp}, for $M(OH)_2$ at 25°C.

$[M^{2+}] = \frac{1}{2}[OH^-] = \frac{1}{2}(1.4 \times 10^{-5}\ M) = 7.0 \times 10^{-6}\ M$ $K_{sp} = [M^{2+}]\,[OH^-]^2 = (7.0 \times 10^{-6})(1.4 \times 10^{-5})^2$ $= 1.4 \times 10^{-15}$	1 point is earned for the correct relationship between $[M^{2+}]$ and $[OH^-]$. 1 point is earned for the correct value.

(c) For the metal carbonate, MCO_3, the value of the solubility-product constant, K_{sp}, is 7.4×10^{-14} at 25°C. On the basis of this information and your results in part (b), which compound, $M(OH)_2$ or MCO_3, has the greater molar solubility in water at 25°C ? Justify your answer with a calculation.

For $M(OH)_2$: $[M^{2+}]$ and molar solubility $= 7.0 \times 10^{-6}\ M$ For MCO_3: $K_{sp} = 7.4 \times 10^{-14} = [M^{2+}][CO_3^{2-}]$ $[M^{2+}]$ and molar solubility $= 2.7 \times 10^{-7}\ M$ Because $7.0 \times 10^{-6}\ M > 2.7 \times 10^{-7}\ M$, $M(OH)_2$ has the greater molar solubility.	1 point is earned for the molar solubility of MCO_3. 1 point is earned for an answer consistent with the calculated molar solubility.

Question 1 (continued)

(d) MCO_3 decomposes at high temperatures, as shown by the reaction represented below.

$$MCO_3(s) \rightleftarrows MO(s) + CO_2(g)$$

A sample of MCO_3 is placed in a previously evacuated container, heated to 423 K, and allowed to come to equilibrium. Some solid MCO_3 remains in the container. The value of K_p for the reaction at 423 K is 0.0012.

(i) Write the equilibrium-constant expression for K_p of the reaction.

$K_p = P_{CO_2}$	1 point is earned for the correct expression.

(ii) Determine the pressure, in atm, of $CO_2(g)$ in the container at equilibrium at 423 K.

$P_{CO_2} = 0.0012$ atm	1 point is earned for the correct pressure.

(iii) Indicate whether the value of $\Delta G°$ for the reaction at 423 K is positive, negative, or zero. Justify your answer.

$\Delta G° = -RT \ln K$ $K = 0.0012 < 1$, thus $\ln K$ is negative; therefore $\Delta G°$ is positive.	1 point is earned for the correct answer with justification.

Question 2
(9 points)

An 8.55 mol sample of methanol, CH_3OH, is placed in a 15.0 L evacuated rigid tank and heated to 327°C. At that temperature, all of the methanol is vaporized and some of the methanol decomposes to form carbon monoxide gas and hydrogen gas, as represented in the equation below.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\,H_2(g)$$

(a) The reaction mixture contains 6.30 mol of $CO(g)$ at equilibrium at 327°C.

(i) Calculate the number of moles of $H_2(g)$ in the tank.

$6.30 \text{ mol CO} \times \frac{2 \text{ mol } H_2}{1 \text{ mol CO}} = 12.6 \text{ mol } H_2$	1 point is earned for the correct number of moles.

(ii) Calculate the number of grams of $CH_3OH(g)$ remaining in the tank.

$6.30 \text{ mol CO} \times \frac{1 \text{ mol } CH_3OH}{1 \text{ mol CO}} = 6.30 \text{ mol } CH_3OH \text{ reacted}$ $8.55 \text{ mol } CH_3OH_{initial} - 6.30 \text{ mol } CH_3OH_{reacted} = 2.25 \text{ mol } CH_3OH$ $2.25 \text{ mol} \times \frac{32.042 \text{ g}}{1 \text{ mol}} = 72.1 \text{ g}$	1 point is earned for the correct number of grams.

(iii) Calculate the mole fraction of $H_2(g)$ in the tank.

$\frac{12.6 \text{ mol } H_2}{2.25 \text{ mol } CH_3OH + 6.30 \text{ mol CO} + 12.6 \text{ mol } H_2}$ $= \frac{12.6}{21.15} = 0.596$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

(iv) Calculate the total pressure, in atm, in the tank at 327°C.

$PV = nRT \Rightarrow P = \frac{nRT}{V}$ $= \frac{(21.15 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(600 \text{ K})}{15.0 \text{ L}}$ $= 69.5 \text{ atm}$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

Question 2 (continued)

(b) Consider the three gases in the tank at 327°C: $CH_3OH(g)$, $CO(g)$, and $H_2(g)$.

(i) How do the average kinetic energies of the molecules of the gases compare? Explain.

The average kinetic energies are the same because all three gases are at the same temperature.	1 point is earned for the correct answer and explanation.

(ii) Which gas has the highest average molecular speed? Explain.

$KE = \frac{1}{2}mv^2$, so at a given temperature the molecules with the lowest mass have the highest average speed. Therefore the molecules in H_2 gas have the highest average molecular speed.	1 point is earned for the correct answer and explanation.

(c) The tank is cooled to 25°C, which is well below the boiling point of methanol. It is found that small amounts of $H_2(g)$ and $CO(g)$ have dissolved in the liquid CH_3OH. Which of the two gases would you expect to be more soluble in methanol at 25°C? Justify your answer.

The only attractive forces between molecules of H_2 and CH_3OH would be due to weak London dispersion forces (LDFs). In contrast, the LDFs are stronger between CO molecules and CH_3OH molecules because CO has more electrons than H_2. In addition CO is slightly polar; thus intermolecular dipole-dipole attractions can form between CO molecules and CH_3OH molecules. With stronger intermolecular interactions between molecules of CO and CH_3OH, CO would be expected to be more soluble in CH_3OH than H_2.	1 point is earned for the correct answer and justification.

Question 3
(9 points)

Answer the following questions about glucose, $C_6H_{12}O_6$, an important biochemical energy source.

(a) Write the empirical formula of glucose.

CH_2O	1 point is earned for the correct formula.

In many organisms, glucose is oxidized to carbon dioxide and water, as represented by the following equation.

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

A 2.50 g sample of glucose and an excess of $O_2(g)$ were placed in a calorimeter. After the reaction was initiated and proceeded to completion, the total heat released by the reaction was calculated to be 39.0 kJ.

(b) Calculate the value of $\Delta H°$, in kJ mol^{-1}, for the combustion of glucose.

$2.50\text{ g} \times \dfrac{1\text{ mol } C_6H_{12}O_6}{180.16\text{ g } C_6H_{12}O_6} = 0.0139\text{ mol } C_6H_{12}O_6$ $\dfrac{-39.0\text{ kJ}}{0.0139\text{ mol}} = -2{,}810\text{ kJ mol}^{-1}$	1 point is earned for the correct answer.

(c) When oxygen is not available, glucose can be oxidized by fermentation. In that process, ethanol and carbon dioxide are produced, as represented by the following equation.

$$C_6H_{12}O_6(s) \rightarrow 2\ C_2H_5OH(l) + 2\ CO_2(g) \qquad \Delta H° = -68.0\text{ kJ mol}^{-1}\text{ at 298 K}$$

The value of the equilibrium constant, K_p, for the reaction at 298 K is 8.9×10^{39}.

(i) Calculate the value of the standard free-energy change, $\Delta G°$, for the reaction at 298 K. Include units with your answer.

$\Delta G° = -RT \ln K$ $= -(8.31\text{ J mol}^{-1}\text{ K}^{-1})(298\text{ K})(\ln 8.9 \times 10^{39})$ $= -228{,}000\text{ J mol}^{-1} = -228\text{ kJ mol}^{-1}$	1 point is earned for correct setup. 1 point is earned for correct answer.

Question 3 (continued)

(ii) Calculate the value of the standard entropy change, $\Delta S°$, in J K^{-1} mol^{-1}, for the reaction at 298 K.

$\Delta G° = \Delta H° - T\Delta S°$ $\Delta S° = \dfrac{\Delta H° - \Delta G°}{T}$ $= \dfrac{(-68.0 \text{ kJ mol}^{-1}) - (-228 \text{ kJ mol}^{-1})}{298 \text{ K}}$ $= 0.537 \text{ kJ K}^{-1} \text{ mol}^{-1} = 537 \text{ J K}^{-1} \text{ mol}^{-1}$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

(iii) Indicate whether the equilibrium constant for the fermentation reaction increases, decreases, or remains the same if the temperature is increased. Justify your answer.

$\Delta H°$ is negative, so when the temperature increases, the equilibrium for the reaction is shifted to the left (according to Le Châtelier's principle). This means that the equilibrium constant decreases.	1 point is earned for the correct answer with justification.

(d) Using your answer for part (b) and the information provided in part (c), calculate the value of $\Delta H°$ for the following reaction.

$$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$$

$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$ $\quad \Delta H° = -2{,}810 \text{ kJ mol}^{-1}$ $2\ C_2H_5OH(l) + 2\ CO_2(g) \rightarrow C_6H_{12}O_6(s)$ $\quad \Delta H° = 68.0 \text{ kJ mol}^{-1}$ ——————————————— $2\ C_2H_5OH(l) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l)$ $\quad \Delta H° = -2{,}740 \text{ kJ mol}^{-1}$, thus $\Delta H°$ for the reaction as written in (d) is $-1{,}370 \text{ kJ mol}^{-1}$.	1 point is earned for the correct setup. 1 point is earned for the correct answer.

Question 4
(15 points)

(a) Zinc metal is added to a hydrobromic acid solution.

Balanced equation: $Zn + 2\ H^+ \rightarrow Zn^{2+} + H_2$	1 point is earned for the correct reactants. 2 points are earned for the correct products. 1 point is earned for the balanced equation.

(ii) Write the oxidation half-reaction for the reaction.

$Zn \rightarrow Zn^{2+} + 2\ e^-$	1 point is earned for the balanced half-reaction.

(b) Solid lithium oxide is added to distilled water.

Balanced equation: $Li_2O + H_2O \rightarrow 2\ Li^+ + 2\ OH^-$	1 point is earned for the correct reactants. 2 points are earned for the correct products. 1 point is earned for the balanced equation.

(ii) Indicate whether the pH of the resulting solution is less than 7, equal to 7, or greater than 7. Explain.

The pH of the resulting solution would be greater than 7 because OH^-, a strong base, is formed in the reaction.	1 point is earned for the correct answer.

(c) A 100 mL sample of 1 *M* strontium chloride solution is mixed with a 100 mL sample of 1 *M* sodium carbonate solution, resulting in the formation of a precipitate.

Balanced equation: $Sr^{2+} + CO_3^{2-} \rightarrow SrCO_3$	2 points are earned for the correct reactants. 1 point is earned for the correct product. 1 point is earned for the balanced equation.

(ii) Describe what will occur if the precipitate is dried and a few drops of 1 *M* hydrochloric acid are added. Explain.

The precipitate disappears and bubbles of CO_2 form.	1 point is earned for a correct answer.

Question 5
(9 points)

A student is instructed to prepare 100.0 mL of 1.250 *M* NaOH from a stock solution of 5.000 *M* NaOH. The student follows the proper safety guidelines.

(a) Calculate the volume of 5.000 *M* NaOH needed to accurately prepare 100.0 mL of 1.250 *M* NaOH solution.

$M_1V_1 = M_2V_2$ $V_1 = \frac{M_2V_2}{M_1} = \frac{(1.250\ M)(100.0\ \text{mL})}{5.000\ M} = 25.00\ \text{mL}$	1 point is earned for the correct volume.

(b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 *M* NaOH solution using 5.000 *M* NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H_2O	Crucible

Pipet 25.00 mL of 5.000 *M* NaOH solution into the 100 mL volumetric flask. Fill the volumetric flask to the calibration line with distilled water; using an eyedropper for the last few drops is advised. Cap the volumetric flask and invert several times to ensure homogeneity.	1 point is earned for descriptions of any <u>two</u> of the three steps. An additional point is earned if all <u>three</u> steps are described.

(c) The student is given 50.0 mL of a 1.00 *M* solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 *M* NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

(i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

When a weak acid is titrated with a strong base, the reaction forms water and the A^- ion. $HA + OH^- \rightleftarrows A^- + H_2O$ The A^- ion formed in the titration reacts with the solvent water to release OH^- ions, making the solution basic at the equivalence point. $A^- + H_2O \rightleftarrows HA + OH^-$	1 point is earned for either the correct equation or a clear statement that the conjugate base, A^-, is a (weak) base. 1 point is earned for indicating that the solution is basic because of the formation of OH^-.

Question 5 (continued)

(ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pK_a
Methyl red	5
Bromothymol blue	7
Phenolphthalein	9

Because the pH is basic at the equivalence point, it is best to use an indicator that changes color in basic solution. Therefore, phenolphthalein would be the best indicator for the titration.	1 point is earned for an answer consistent with the answer to part (c)(i) with justification.

(d) The student is given another 50.0 mL sample of 1.00 *M* HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.

(i) What is the value of the acid-dissociation constant, K_a, for the weak acid? Explain your reasoning.

The resulting solution is at the half-equivalence-point, where $[HA] = [A^-]$, thus $pH = pK_a = 5.0 \Rightarrow K_a = 1 \times 10^{-5}$.	1 point is earned for showing that the system is at the half-equivalence point. 1 point is earned for the correct value of K_a.

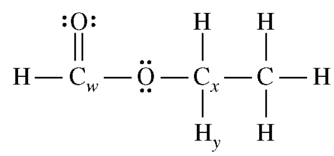
(ii) Explain why the addition of a few drops of 1.250 *M* NaOH to the resulting solution does not appreciably change its pH.

The resulting solution is a buffer; therefore adding a few drops of acid or base does not appreciably change the pH.	1 point is earned for indicating that the solution is a buffer.

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.

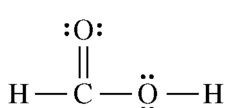
(ii) Estimate the numerical value of the H_y–C_x–O bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

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.

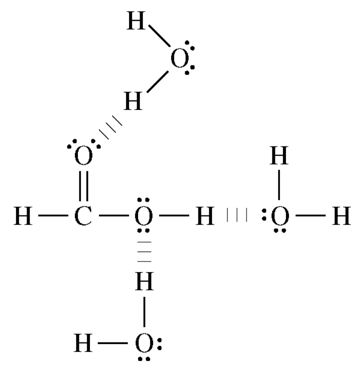
$$C_2H_5OH(l) + HCOOH(l) \rightleftarrows CH_3CH_2OCHO(l) + H_2O(l)$$

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

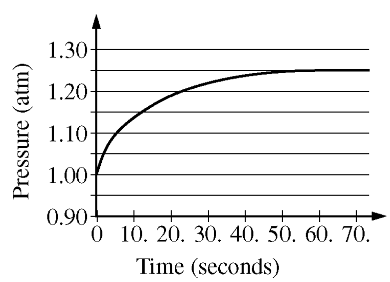
	1 point is earned for a correct diagram.

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.

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.