AP® Chemistry
2010 Scoring Guidelines

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Question 1
(10 points)

Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product-constant, K_{sp}, is 5.0×10^{-13} at 298 K.

(a) Write the expression for the solubility-product constant, K_{sp}, of AgBr.

$K_{sp} = [Ag^+][Br^-]$	One point is earned for the correct expression (ion charges must be present; parentheses instead of square brackets not accepted).

(b) Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

Let x = equilibrium concentration of Ag^+ (and of Br^-). Then $K_{sp} = 5.0 \times 10^{-13} = x^2 \Rightarrow x = 7.1 \times 10^{-7}\,M$	One point is earned for the correct value with supporting work (units not necessary).

(c) A 50.0 mL sample of distilled water is added to the solution described in part (b), which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part (b) ? Justify your answer.

The value of $[Ag^+]$ after addition of distilled water is equal to the value in part (b). The concentration of ions in solution in equilibrium with a solid does <u>not</u> depend on the volume of the solution.	One point is earned for the correct answer with justification.

(d) Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(*s*) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}.)

$5.0 \text{ g AgBr} \times \frac{1 \text{ mol AgBr}}{188 \text{ g AgBr}} = 0.0266 \text{ mol AgBr}$	One point is earned for the calculation of moles of dissolved AgBr.
$\frac{0.0266 \text{ mol}}{V} = 7.1 \times 10^{-7} \text{mol L}^{-1} \Rightarrow V = 3.7 \times 10^4 \text{ L}$	One point is earned for the correct answer for the volume of water

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Question 1 (continued)

(e) A student mixes 10.0 mL of 1.5×10^{-4} *M* $AgNO_3$ with 2.0 mL of 5.0×10^{-4} *M* NaBr and stirs the resulting mixture. What will the student observe? Justify your answer with calculations.

$[Ag^+] = \frac{(10.0\text{ mL})(1.5 \times 10^{-4}\ M)}{12.0\text{ mL}} = 1.3 \times 10^{-4}\ M$ $[Br^-] = \frac{(2.0\text{ mL})(5.0 \times 10^{-4} M)}{12.0\text{ mL}} = 8.3 \times 10^{-5}\ M$ $Q = [Ag^+][Br^-] = (1.3 \times 10^{-4}\ M)(8.3 \times 10^{-5}\ M) = 1.1 \times 10^{-8}$ $1.1 \times 10^{-8} > 5.0 \times 10^{-13}$, ∴ a precipitate will form.	One point is earned for calculation of concentration of ions. One point is earned for calculation of Q and conclusion based on comparison between Q and K_{sp}. One point is earned for indicating the precipitation of AgBr.

(f) The color of another salt of silver, AgI(*s*), is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

(i) Write the chemical equation for the reaction that occurred in the test tube.

$AgBr(s) + I^-(aq) \rightarrow AgI(s) + Br^-(aq)$ ***OR*** $AgBr(s) + NaI(aq) \rightarrow AgI(s) + NaBr(aq)$	One point is earned for the correct equation.

(ii) Which salt has the greater value of K_{sp}: AgBr or AgI ? Justify your answer.

AgBr has the greater value of K_{sp}. The precipitate will consist of the less soluble salt when both $I^-(aq)$ and $Br^-(aq)$ are present. Because the color of the precipitate in the test tube turns yellow, it must be AgI(*s*) that precipitates; therefore K_{sp} for AgBr must be greater than K_{sp} for AgI. ***OR*** K_{eq} for the displacement reaction is $\frac{K_{sp}\text{ of AgBr}}{K_{sp}\text{ of AgI}}$. Because yellow AgI forms, $K_{eq} > 1$; therefore K_{sp} of AgBr > K_{sp} of AgI.	One point is earned for the correct choice with justification.

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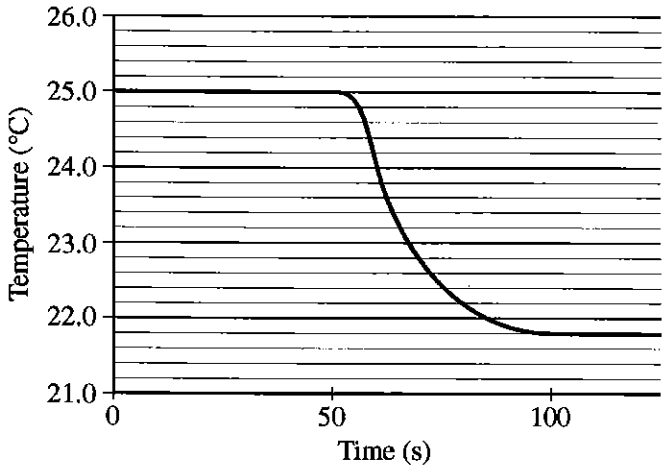
Question 2
(10 points)

A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



(1) (a) Determine the change in temperature of the solution that results from the dissolution of the urea.

$\Delta T = 21.8 - 25.0 = -3.2$ Celsius degrees	One point is earned for the correct temperature change.

(1) (b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

The process is endothermic. The decrease in temperature indicates that the process for the dissolution of urea in water requires energy.	One point is earned for the correct choice with justification.

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Question 2 (continued)

(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g^{-1} $°C^{-1}$ throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

Assuming that no heat energy is lost from the calorimeter and given that the calorimeter has a negligible heat capacity, the sum of the heat of dissolution, q_{soln} and the change in heat energy of the urea-water mixture must equal zero. $q_{soln} + mc\Delta T = 0 \quad \Rightarrow \quad q_{soln} = -mc\Delta T$ $m_{soln} = 5.13\text{ g} + 91.95\text{ g} = 97.08\text{ g}$ $q_{soln} = -(97.08\text{ g})(4.2\text{ J g}^{-1}\text{°C}^{-1})(-3.2\text{°C}) = 1.3 \times 10^3\text{ J}$	One point is earned for the correct setup. One point is earned for the correct numerical result for the heat of dissolution.

(ii) Calculate the molar enthalpy of solution, ΔH°_{soln}, of urea in kJ mol^{-1}.

$\Delta H^\circ_{soln} = \dfrac{q_{soln}}{\text{mol solute}}$ molar mass of urea $= 4(1.0) + 2(14.0) + 12.0 + 16.0 = 60.0\text{ g mol}^{-1}$ moles of urea $= 5.13\text{ g urea} \times \dfrac{1\text{ mol urea}}{60.0\text{ g urea}} = 0.0855\text{ mol}$ $\Delta H^\circ_{soln} = \dfrac{1.3 \times 10^3\text{ J}}{0.0855\text{ mol}} = 1.5 \times 10^4\text{ J mol}^{-1} = 15\text{ kJ mol}^{-1}$	One point is earned for the calculation of moles of urea. One point is earned for the correct numerical result with correct algebraic sign.

(d) Using the information in the table below, calculate the value of the molar entropy of solution, ΔS°_{soln}, of urea at 298 K. Include units with your answer.

	Accepted Value
ΔH°_{soln} of urea	14.0 kJ mol^{-1}
ΔG°_{soln} of urea	−6.9 kJ mol^{-1}

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $-6.9\text{ kJ mol}^{-1} = 14.0\text{ kJ mol}^{-1} - (298\text{ K})(\Delta S^\circ)$ $\Delta S^\circ_{soln} = 0.0701\text{ kJ mol}^{-1}\text{ K}^{-1} = 70.1\text{ J mol}^{-1}\text{ K}^{-1}$	One point is earned for the correct setup. One point is earned for the correct numerical result with correct units.

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Question 2 (continued)

(e) The student repeats the experiment and this time obtains a result for ΔH°_{soln} of urea that is 11 percent below the accepted value. Calculate the value of ΔH°_{soln} that the student obtained in this second trial.

Error = $(0.11)(14.0\ \text{kJ mol}^{-1}) = 1.54\ \text{kJ mol}^{-1}$ $14.0\ \text{kJ mol}^{-1} - 1.54\ \text{kJ mol}^{-1} = 12.5\ \text{kJ mol}^{-1}$	One point is earned for the correct numerical result.

(f) The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5°C. What effect, if any, would using the cold urea instead of urea at 25°C have on the experimentally obtained value of ΔH°_{soln} ? Justify your answer.

There would be an increase in the obtained value for ΔH°_{soln} because the colder urea would have caused a larger negative temperature change.	One point is earned for the correct prediction with justification.

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Question 3
(9 points)

$$8\ H^+(aq) + 4\ Cl^-(aq) + MnO_4^-(aq) \rightarrow 2\ Cl_2(g) + Mn^{3+}(aq) + 4\ H_2O(l)$$

$Cl_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

(a) A 25.00 mL sample of 0.250 *M* NaCl reacts completely with excess $KMnO_4(aq)$. The $Cl_2(g)$ produced is dried and stored in a sealed container. At 22°C the pressure of the $Cl_2(g)$ in the container is 0.950 atm.

(i) Calculate the number of moles of $Cl^-(aq)$ present before any reaction occurs.

$\text{mol } Cl^- = (0.02500\text{ L})(0.250\ M) = 6.25 \times 10^{-3}\text{ mol}$	One point is earned for the correct numerical value.

(ii) Calculate the volume, in L, of the $Cl_2(g)$ in the sealed container.

$\text{mol } Cl_2 = \frac{\text{mol } Cl^-}{2} = \frac{6.25 \times 10^{-3}\text{ mol}}{2} = 3.125 \times 10^{-3}\text{ mol } Cl_2$ $V = \frac{nRT}{P} = \frac{(3.125 \times 10^{-3}\text{ mol } Cl_2)(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(295\text{ K})}{0.950\text{ atm}}$ $= 0.0797\text{ L } Cl_2$	One point is earned for the correct number of moles of Cl_2 based on stoichiometry. One point is earned for substitution into ideal gas law and correct numerical result.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of Disappearance of MnO_4^- in $M\,s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

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Question 3 (continued)

(b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.

(i) Cl^-

The reaction is second order. Tripling $[Cl^-]$ between trials 1 and 2 with no change in $[MnO_4^-]$ results in a nine-fold increase in the rate: $\left(\frac{0.0312\ M}{0.0104\ M}\right)^x = \frac{2.03 \times 10^{-7}}{2.25 \times 10^{-8}}$ $3^x = 9$ $x = 2$ Thus the order of the reaction must be 2 with respect to Cl^-.	One point is earned for the correct order of reaction with justification.

(ii) MnO_4^-

The reaction is first order. Doubling $[MnO_4^-]$ between trials 3 and 2 with no change in $[Cl^-]$ results in a doubling of the rate: $\left(\frac{0.00400\ M}{0.00200\ M}\right)^y = \frac{2.03 \times 10^{-7}}{1.02 \times 10^{-7}}$ $2^y = 2$ $y = 1$ Thus the order of the reaction must be 1 with respect to MnO_4^-.	One point is earned for the correct order of reaction with justification.

(c) The reaction is known to be third order with respect to H^+. Using this information and your answers to part (b) above, complete both of the following:

(i) Write the rate law for the reaction.

rate = $k[Cl^-]^2[MnO_4^-][H^+]^3$	One point is earned for the correct rate law.

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Question 3 (continued)

(ii) Calculate the value of the rate constant, k, for the reaction, including appropriate units.

Using data from trial 1: $2.25 \times 10^{-8}\ M\,s^{-1} = k(0.0104\ M)^2(0.00400\ M)(3.00\ M)^3$ $k = 1.93 \times 10^{-3}\ M^{-5}s^{-1}$	One point is earned for the correct numerical result. One point is earned for the correct units.

(d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

It is not likely that the reaction occurs in a single step because the orders of the reaction with respect to the reactants do not correspond to the coefficients in the balanced equation ***OR*** It is not likely that the reaction occurs in a single step because the reaction requires the collision of many (13) reactant particles and the frequency of a 13-particle collision is negligible.	One point is earned for the correct answer with justification.

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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 0.2 *M* potassium hydroxide solution is titrated with a 0.1 *M* nitric acid solution.

(i) Balanced equation: $H_3O^+ + OH^- \rightarrow 2\,H_2O$ ***OR*** $H^+ + OH^- \rightarrow H_2O$	One point is earned for each correct reactant. One point is earned for the correct product. One point is earned for correctly balancing (mass and charge) the equation.

(ii) What would be observed if the solution was titrated well past the equivalence point using bromthymol blue as the indicator? (Bromthymol blue is yellow in acidic solution and blue in basic solution.)

The solution would appear yellow.	One point is earned for the correct description of the solution.

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Question 4 (continued)

(b) Propane is burned completely in excess oxygen gas.

(i) Balanced equation: $C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$	One point is earned for both correct reactants. Two points are earned for the correct products. One point is earned for correctly balancing the equation.

(ii) When the products of the reaction are bubbled through distilled water, is the resulting solution neutral, acidic, or basic? Explain.

The resulting solution would be acidic because CO_2 reacts with water as a weak acid.	One point is earned for the correct choice with justification.

(c) A solution of hydrogen peroxide is heated, and a gas is produced.

(i) Balanced equation: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$	One point is earned for the correct reactant. Two points are earned for the correct products. One point is earned for correctly balancing the equation.

(ii) Identify the oxidation state of oxygen in hydrogen peroxide.

The oxidation state of O in H_2O_2 is -1.	One point is earned for the correct oxidation state.

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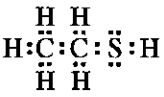
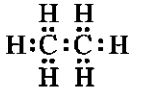
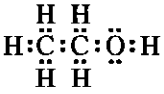
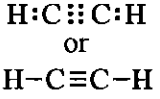
Question 5
(8 points)

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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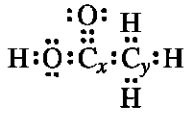
Question 5 (continued)

(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.

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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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Question 6
(9 points)

$$2\ Al(s) + 3\ Zn^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Zn(s)$$

Respond to the following statements and questions that relate to the species and the reaction represented above.

(a) Write the complete electron configuration (e.g., $1s^2\,2s^2\ldots$) for Zn^{2+}.

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$	One point is earned for the correct configuration.

(b) Which species, Zn or Zn^{2+}, has the greater ionization energy? Justify your answer.

Zn^{2+} has the greater ionization energy. The electron being removed from Zn^{2+} experiences a larger effective nuclear charge than the electron being removed from Zn because Zn^{2+} has two fewer electrons shielding the nucleus. ***OR*** It takes more energy to remove a negatively charged electron from a positive ion than from a neutral atom.	One point is earned for identifying Zn^{2+} with justification.

(c) Identify the species that is oxidized in the reaction.

Al(*s*)	One point is earned for identifying Al.

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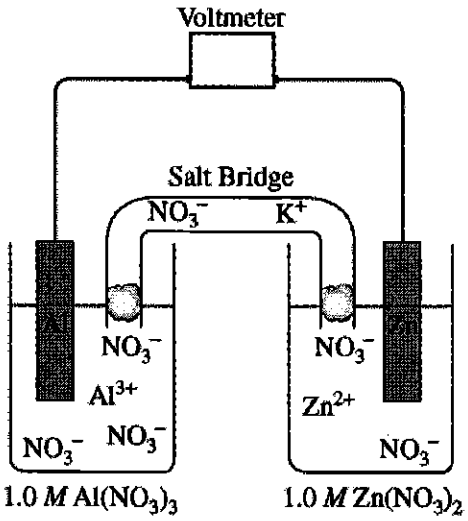
Question 6 (continued)

The diagram below shows a galvanic cell based on the reaction. Assume that the temperature is 25°C.



1 (d) The diagram includes a salt bridge that is filled with a saturated solution of KNO_3. Describe what happens in the salt bridge as the cell operates.

As the cell operates, NO_3^- ions flow toward the Al half-cell and K^+ ions flow toward the Zn half-cell.	One point is earned for correctly indicating the direction of ion flow.

1 (e) Determine the value of the standard voltage, $E°$, for the cell.

$E° = (-0.76\text{ V}) - (-1.66\text{ V}) = 0.90\text{ V}$	One point is earned for the correct $E°$.

2 (f) Indicate whether the value of the standard free-energy change, $\Delta G°$, for the cell reaction is positive, negative, or zero. Justify your answer.

$\Delta G°$ is negative since $E°$ is positive and $\Delta G° = -n\mathcal{F}E°$. ***OR*** $\Delta G°$ must be negative because the reaction is spontaneous under standard conditions.	One point is earned for indicating that $\Delta G°$ is negative. One point is earned for a correct justification.

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Question 6 (continued)

(b) (g) If the concentration of $Al(NO_3)_3$ in the $Al(s)/Al^{3+}(aq)$ half-cell is lowered from 1.0 M to 0.01 M at 25°C, does the cell voltage increase, decrease, or remain the same? Justify your answer.

Lowering $[Al^{3+}]$ causes an increase in the cell voltage. The value of Q will fall below 1.0 and the log term in the Nernst equation will become negative. This causes the value of E_{cell} to become more positive.	One point is earned for indicating that E_{cell} increases.
OR	
A decrease in a product concentration will increase the spontaneity of the reaction, increasing the value of E_{cell}.	One point is earned for the correct justification.