CHEMISTRY
Section II
(Total time—90 minutes)

Part A
Time—40 minutes
YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

1. Answer the following questions relating to the solubilities of two silver compounds, Ag_2CrO_4 and Ag_3PO_4.

Silver chromate dissociates in water according to the equation shown below.

$$Ag_2CrO_4(s) \rightleftarrows 2\,Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = 2.6 \times 10^{-12} \text{ at } 25°C$$

(a) Write the equilibrium-constant expression for the dissolving of $Ag_2CrO_4(s)$.

(b) Calculate the concentration, in mol L^{-1}, of $Ag^+(aq)$ in a saturated solution of Ag_2CrO_4 at 25°C.

(c) Calculate the maximum mass, in grams, of Ag_2CrO_4 that can dissolve in 100. mL of water at 25°C.

(d) A 0.100 mol sample of solid $AgNO_3$ is added to a 1.00 L saturated solution of Ag_2CrO_4. Assuming no volume change, does $[CrO_4^{2-}]$ increase, decrease, or remain the same? Justify your answer.

In a saturated solution of Ag_3PO_4 at 25°C, the concentration of $Ag^+(aq)$ is 5.3×10^{-5} M. The equilibrium-constant expression for the dissolving of $Ag_3PO_4(s)$ in water is shown below.

$$K_{sp} = [Ag^+]^3[PO_4^{3-}]$$

(e) Write the balanced equation for the dissolving of Ag_3PO_4 in water.

(f) Calculate the value of K_{sp} for Ag_3PO_4 at 25°C.

(g) A 1.00 L sample of saturated Ag_3PO_4 solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is $[Ag^+]$ in the solution? Justify your answer.

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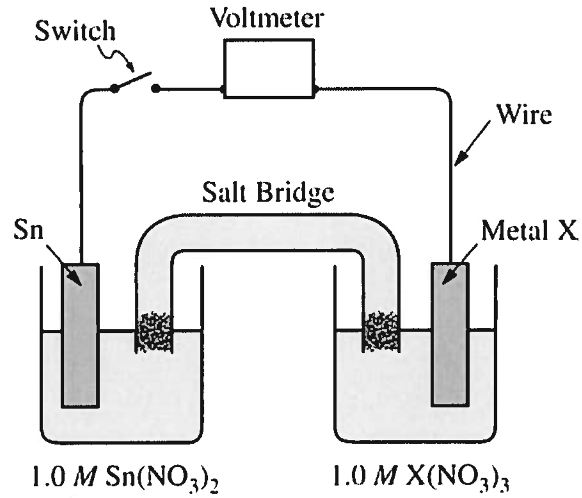

6. An electrochemical cell is constructed with an open switch, as shown in the diagram above. A strip of Sn and a strip of an unknown metal, X, are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The half-reactions are shown below.

$$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s) \qquad E° = -0.14\text{ V}$$

$$X^{3+}(aq) + 3\,e^- \rightarrow X(s) \qquad E° = ?$$

(a) In the diagram above, label the electrode that is the cathode. Justify your answer.

(b) In the diagram above, draw an arrow indicating the direction of the electron flow in the external circuit when the switch is closed.

(c) If the standard cell potential, $E°_{cell}$, is +0.60 V, what is the standard reduction potential, in volts, for the X^{3+}/X electrode?

(d) Identify metal X.

(e) Write a balanced net-ionic equation for the overall chemical reaction occurring in the cell.

(f) In the cell, the concentration of Sn^{2+} is changed from 1.0 *M* to 0.50 *M*, and the concentration of X^{3+} is changed from 1.0 *M* to 0.10 *M*.

(i) Substitute all the appropriate values for determining the cell potential, E_{cell}, into the Nernst equation. (Do not do any calculations.)

(ii) On the basis of your response in part (f) (i), will the cell potential, E_{cell}, be greater than, less than, or equal to the original $E°_{cell}$? Justify your answer.

Answer EITHER Question 7 below OR Question 8 printed on page 13. Only one of these two questions will be graded. If you start both questions, be sure to cross out the question you do not want graded. The Section II score weighting for the question you choose is 15 percent.

7. Use appropriate chemical principles to account for each of the following observations. In each part, your response <u>must</u> include specific information about <u>both</u> substances.

   (a) At 25°C and 1 atm, F_2 is a gas, whereas I_2 is a solid.

   (b) The melting point of NaF is 993°C, whereas the melting point of CsCl is 645°C.

   (c) The shape of the ICl_4^- ion is square planar, whereas the shape of the BF_4^- ion is tetrahedral.

   (d) Ammonia, NH_3, is very soluble in water, whereas phosphine, PH_3, is only moderately soluble in water.

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Question 1

Answer the following questions relating to the solubilities of two silver compounds, Ag_2CrO_4 and Ag_3PO_4.

Silver chromate dissociates in water according to the equation shown below.

$$Ag_2CrO_4(s) \rightleftarrows 2\ Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = 2.6 \times 10^{-12} \text{ at } 25°C$$

(a) Write the equilibrium-constant expression for the dissolving of $Ag_2CrO_4(s)$.

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$	1 point for correct expression

(b) Calculate the concentration, in mol L^{-1}, of $Ag^+(aq)$ in a saturated solution of Ag_2CrO_4 at 25°C.

$Ag_2CrO_4(s) \rightleftarrows 2\ Ag^+(aq) + CrO_4^{2-}(aq)$ I – 0 0 C – $+2x$ $+x$ F – $0 + 2x$ $0 + x$	1 point for correct stoichiometry of $Ag^+(aq)$ and $CrO_4^{2-}(aq)$
$2.6 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}]$ $2.6 \times 10^{-12} = [2x]^2[x] = 4x^3$ $8.7 \times 10^{-5} = x = [CrO_4^{2-}]$ $[Ag^+] = 2x = 2 \times (8.7 \times 10^{-5}\ M) = 1.7 \times 10^{-4}\ M$	1 point for substituting and calculating $[Ag^+]$

(c) Calculate the maximum mass, in grams, of Ag_2CrO_4 that can dissolve in 100. mL of water at 25°C.

$\frac{8.7 \times 10^{-5} \text{ mole } Ag_2CrO_4}{1 \text{ L}} \times \frac{331.7 \text{ g}}{1 \text{ mole } Ag_2CrO_4} = \frac{0.029 \text{ g } Ag_2CrO_4}{1 \text{ L}}$ $\frac{0.029 \text{ g } Ag_2CrO_4}{1 \text{ L}} \times 0.100 \text{ L} = 0.0029 \text{ g } Ag_2CrO_4$	1 point for molar mass of Ag_2CrO_4 1 point for mass of Ag_2CrO_4 in 100 mL

Question 1 (cont'd.)

(d) A 0.100 mol sample of solid $AgNO_3$ is added to a 1.00 L saturated solution of Ag_2CrO_4. Assuming no volume change, does $[CrO_4^{2-}]$ increase, decrease, or remain the same? Justify your answer.

The $[CrO_4^{2-}]$ will decrease. Adding $[Ag^+]$ will make Q (nonequilibrium reaction quotient) greater than K. To re-establish equilibrium, the reaction goes from right to left, decreasing the quotient to return to equilibrium.	1 point for correct prediction and explanation in terms of Q or LeChâtelier's principle

In a saturated solution of Ag_3PO_4 at 25°C, the concentration of $Ag^+(aq)$ is 5.3×10^{-5} M. The equilibrium-constant expression for the dissolving of $Ag_3PO_4(s)$ in water is shown below.

$$K_{sp} = [Ag^+]^3[PO_4^{3-}]$$

(e) Write the balanced equation for the dissolving of Ag_3PO_4 in water.

$Ag_3PO_4(s) \rightarrow 3\ Ag^+(aq) + PO_4^{3-}(aq)$	1 point for correct, balanced chemical equation

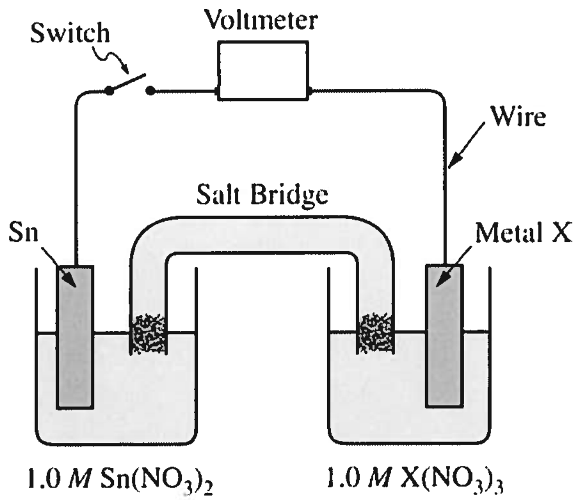
(f) Calculate the value of K_{sp} for Ag_3PO_4 at 25°C.

$[Ag^+] = 5.3 \times 10^{-5}\ M$ $[PO_4^{3-}] = 5.3 \times 10^{-5}\ M\ Ag^+ \times \dfrac{1 \text{ mol } PO_4^{3-}}{3 \text{ mol } Ag^+} = 1.8 \times 10^{-5}\ M$	1 point for correct $[PO_4^{3-}]$
$K_{sp} = [Ag^+]^3[PO_4^{3-}]$ $= (5.3 \times 10^{-5})^3(1.8 \times 10^{-5}) = 2.6 \times 10^{-18}$	1 point for K_{sp}

(g) A 1.00 L sample of saturated Ag_3PO_4 solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is $[Ag^+]$ in the solution? Justify your answer.

$[Ag^+] = 5.3 \times 10^{-5}\ M$ The $[Ag^+]$ in a saturated solution of Ag_3PO_4 is independent of the volume of the solution.	1 point for correct $[Ag^+]$ and explanation

Question 6



An electrochemical cell is constructed with an open switch, as shown in the diagram above. A strip of Sn and a strip of an unknown metal, X, are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The half-reactions are shown below.

$$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s) \qquad E° = -0.14\text{ V}$$

$$X^{3+}(aq) + 3\,e^- \rightarrow X(s) \qquad E° = ?$$

(a) In the diagram above, label the electrode that is the cathode. Justify your answer.

The Sn (tin) electrode is the cathode.	1 point for identifying Sn as the cathode
The increase in mass indicates that reduction occurs at the Sn electrode: $Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)$ Reduction occurs at the cathode.	1 point for reasoning based on increase in mass

(b) In the diagram above, draw an arrow indicating the direction of the electron flow in the external circuit when the switch is closed.

Diagram should have arrow showing electrons flowing from the anode towards the cathode.	1 point for correct direction of electron flow

Question 6 (cont')

(c) If the standard cell potential, E°_{cell}, is +0.60 V, what is the standard reduction potential, in volts, for the X^{3+}/X electrode?

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ $+0.60\text{ V} = -0.14\text{ V} - E^\circ_{anode}$ $E^\circ_{anode} = -0.74\text{ V}$	1 point for correct potential with correct sign

(d) Identify metal X.

Cr	1 point for correct metal

(e) Write a balanced net-ionic equation for the overall chemical reaction occurring in the cell.

$3\ Sn^{2+} + 2\ Cr \rightarrow 3\ Sn + 2\ Cr^{3+}$	1 point for correctly balanced net-ionic equation

(f) In the cell, the concentration of Sn^{2+} is changed from 1.0 *M* to 0.50 *M*, and the concentration of X^{3+} is changed from 1.0 *M* to 0.10 *M*.

(i) Substitute all the appropriate values for determining the cell potential, E_{cell}, into the Nernst equation. (Do not do any calculations.)

$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log \frac{[Cr^{3+}]^2}{[Sn^{2+}]^3}$ $E_{cell} = +0.60\text{ V} - \frac{0.0592}{6} \log \frac{[0.10]^2}{[0.50]^3}$	1 point for using $E^\circ_{cell} = +0.60$ V 1 point for using $n = 6$ 1 point for substituting correctly into the Q expression based on the equation in part (e)

(ii) On the basis of your response in part (f) (i), will the cell potential, E_{cell}, be greater than, less than, or equal to the original E°_{cell}? Justify your answer.

E_{cell} will be greater (more positive). Since the Q ratio is a number less than 1, the log of the ratio will be negative. A negative times a negative is positive. Thus, $-\frac{0.0592}{6} \log \frac{[0.10]^2}{[0.50]^3}$ increases E_{cell}	1 point for the correct prediction with an explanation based on Q

Question 7

Use appropriate chemical principles to account for each of the following observations. In each part, your response must include specific information about both substances.

(a) At 25°C and 1 atm, F_2 is a gas, whereas I_2 is a solid.

Both F_2 and I_2 are nonpolar, so the only intermolecular attractive forces are London dispersion forces. I_2 is solid because the electrons in the I_2 molecule occupy a larger volume and are more polarizable compared to the electrons in the F_2 molecule. As a result, the dispersion forces are considerably stronger in I_2 compared to F_2.	1 point for indicating that both molecules have dispersion forces as IMFs 1 point for indicating that I_2 molecules are more polarizable than F_2 molecules

(b) The melting point of NaF is 993°C, whereas the melting point of CsCl is 645°C.

Both NaF and CsCl are ionic compounds with the same charges on the cations and anions. The ionic radius of Na^+ is smaller than the ionic radius of Cs^+ and the ionic radius of F^- is smaller than the ionic radius of Cl^-. Therefore, the ionic centers are closer in NaF than in CsCl. Melting occurs when the attraction between the cation and the anion are overcome due to thermal motion. Since the lattice energy is inversely proportional to the distance between the ion centers (Coulomb's Law), the compound with the smaller ions will have the stronger attractions and the higher melting point.	1 point for indicating that NaF and CsCl are both ionic compounds (or are composed of M^+ and X^- ions) 1 point for indicating that the strength of these forces is determined by the distance between the ionic centers (or the size of the ions)

(c) The shape of the ICl_4^- ion is square planar, whereas the shape of the BF_4^- ion is tetrahedral.

The central iodine atom in ICl_4^- has four bonding pairs and two lone pairs of electrons on the central iodine atom, so the molecular geometry is square planar. BF_4^- has four bonding pairs and no lone pairs on the central boron atom, so the molecular geometry is tetrahedral.	2 points for indicating that ICl_4^- has two unshared electron pairs, but BF_4^- has no unshared pairs Note: 1 point earned if student gives incorrect numbers of unshared electron pairs but indicates that difference in number of unshared electron pairs determines difference in geometry.

Question 7 (cont'd.)

(d) Ammonia, NH_3, is very soluble in water, whereas phosphine, PH_3, is only moderately soluble in water.

Ammonia has hydrogen-bonding intermolecular forces, whereas phosphine has dipole-dipole and/or dispersion intermolecular forces. Water also has hydrogen-bonding intermolecular attractive forces. Ammonia is more soluble in water than phosphine because ammonia molecules can hydrogen-bond with water molecules, whereas phosphine molecules cannot hydrogen-bond with water molecules.	1 point for indicating that NH_3 can form hydrogen bonds but PH_3 cannot 1 point for indicating that NH_3 can form hydrogen bonds with water, but PH_3 cannot