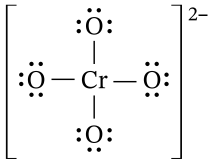
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

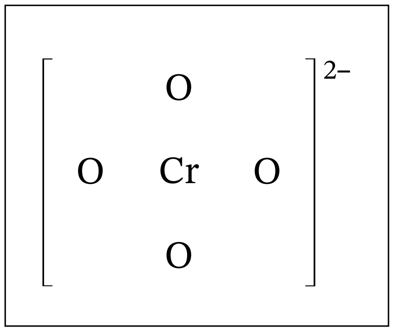
Figure 1



i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

ii. On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of −1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

Figure 2



Part B

When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\,H_3O^+(aq) \rightarrow 2\,CrO_3(aq) + 3\,H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\,H^+(aq) + 6\,e^- \rightarrow Cr(s) + 3\,H_2O(l) \qquad E^\circ = -1.32\text{ V}$$

Part C

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

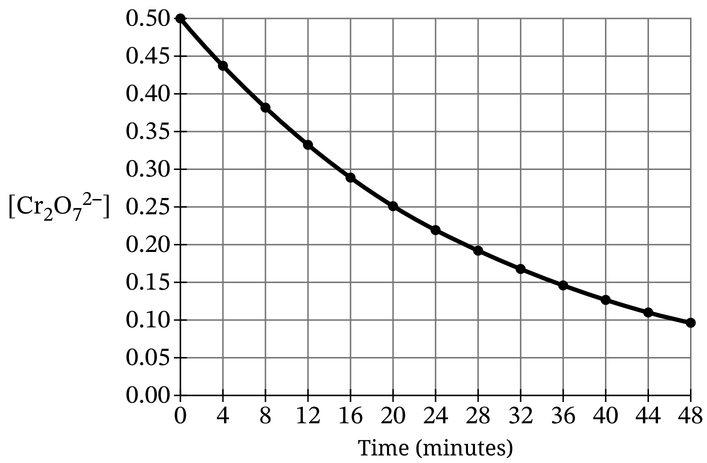
Part D

Calculate the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

In a separate experiment, an iron wire is placed directly in a solution of $0.50\ M\ Cr_2O_7^{2-}(aq)$ with pH = 1.99. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

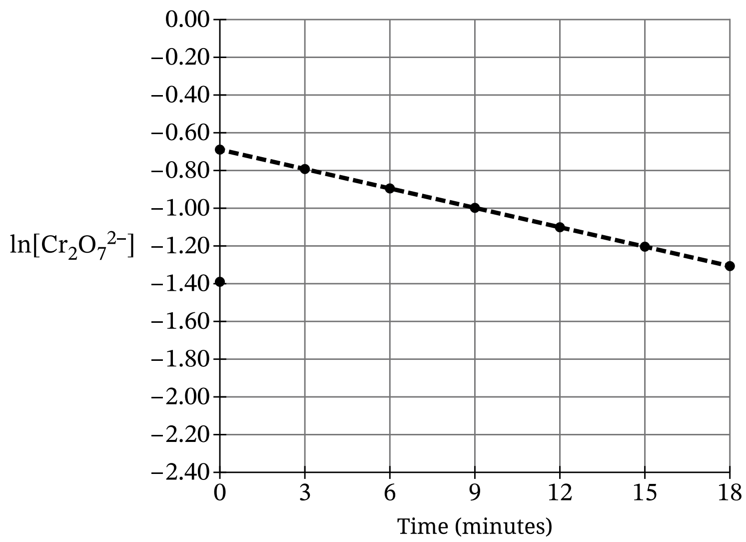


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln[Cr_2O_7^{2-}]$ versus time for a trial with an initial concentration of $0.50\ M\ Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

Figure 4



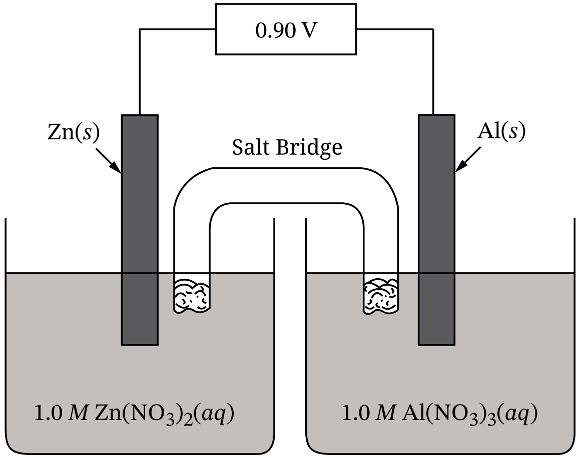
Part F

Calculate the value of the rate constant, k, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

Part G

The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of $0.25\ M\ Cr_2O_7^{2-}(aq)$ instead of $0.50\ M\ Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln[Cr_2O_7^{2-}]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

6. A scientist constructs a galvanic cell as shown in the diagram. As the cell operates, the $Zn(s)$ electrode increases in mass and the $Al(s)$ electrode decreases in mass. A data table with the standard reduction potentials for the substances follows the diagram.



Half-Reaction	E° (V)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66

A. Write the half-reaction for the oxidation that occurs at the anode.

B. Write the balanced net ionic equation for the overall reaction that occurs in the galvanic cell.

C. Initially, each electrode has a mass of 50.0 g. The cell is allowed to run for a period of time and is then stopped. Which electrode's mass changed the most? Justify your answer with a calculation.

Reduction Half-Reaction	E° (V)
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	$+1.50$
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.19
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	-1.85

D. The standard Zn/Al cell has a value of E°_{cell} equal to 0.90 V. The scientist needs a galvanic cell that produces a greater voltage. The scientist has access to the chemical systems in the table. If the scientist uses the Zn half-cell and one of the other options from the table, what is the MAXIMUM voltage that could be generated at standard conditions?

Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2\,Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$$

(a) What are the oxidation numbers of silver in $Ag(s)$ and $Ag_2S(s)$?

$Ag(s)$__________ $Ag_2S(s)$__________

(b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

(i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

(ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $Ag_2S(s)$ (molar mass 247.80 g / mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $Ag_2S(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $Rh(s)$, onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	$E°$ (V)
$Rh^{3+}(aq) + 3\,e^- \rightarrow Rh(s)$	+0.80
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23

(i) Write the balanced net ionic equation for plating $Rh(s)$ from the acidified $Rh_2(SO_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

(e) Calculate the length of time, in seconds, required to plate 2.8 g of $Rh(s)$ onto a piece of sterling silver if 2.0 C / s of current is applied.

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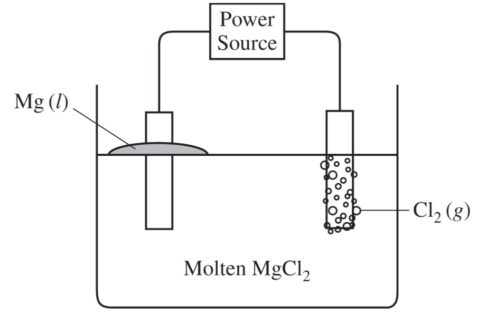

Half-Reaction	$E°$ (V)
$Mg^{2+} + 2\,e^- \rightarrow Mg$	−2.37
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	+ 1.36

5. Molten $MgCl_2$ can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl_2 gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.

(a) Draw an arrow on the diagram to show the direction of electron flow through the external circuit as the cell operates.

(b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of Mg(l) at the cathode?

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CHEMISTRY

Section II

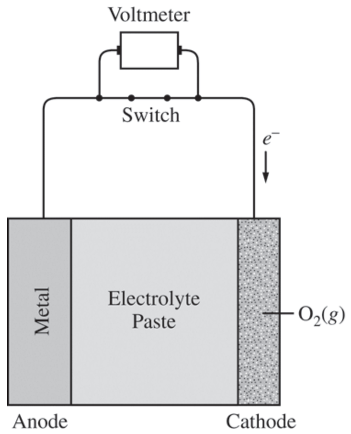
7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.



1. Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	E at pH 11 and 298 K (V)
$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$	+0.34
$ZnO(s) + H_2O(l) + 2\,e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	−1.31
$Na_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Na(s) + 2\,OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\,e^- \rightarrow Ca(s) + 2\,OH^-(aq)$	−2.78

(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\,Zn(s) + O_2(g) \rightarrow 2\,ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

(d) Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?