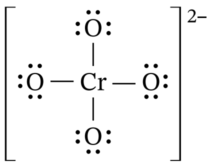
Question 2: Version J

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.

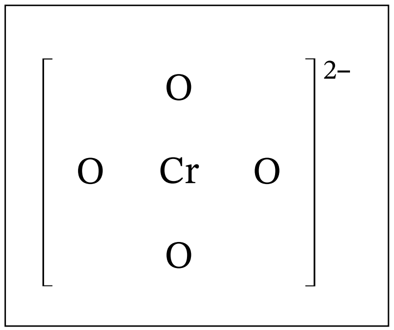
Figure 1



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.

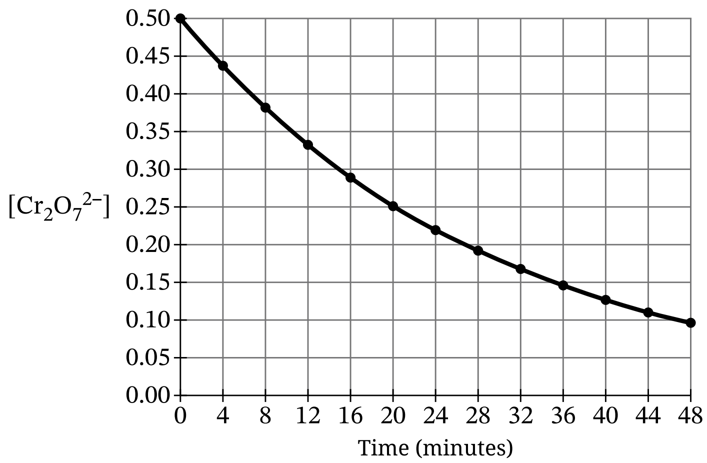
Part D

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

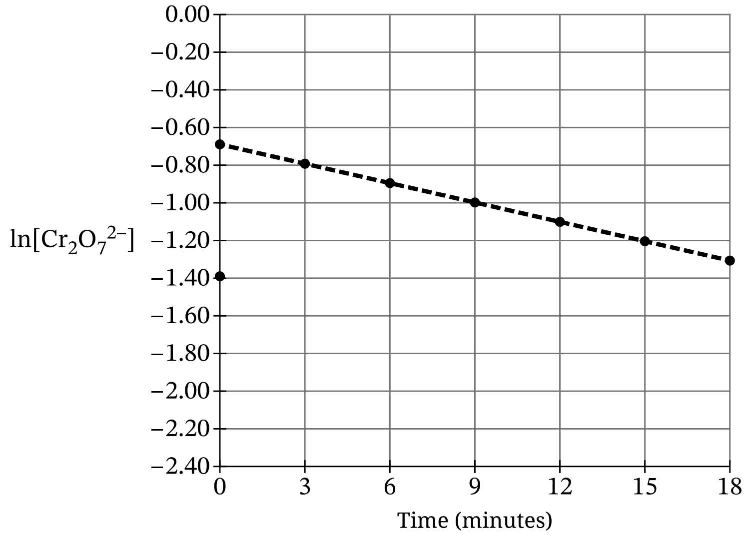


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

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



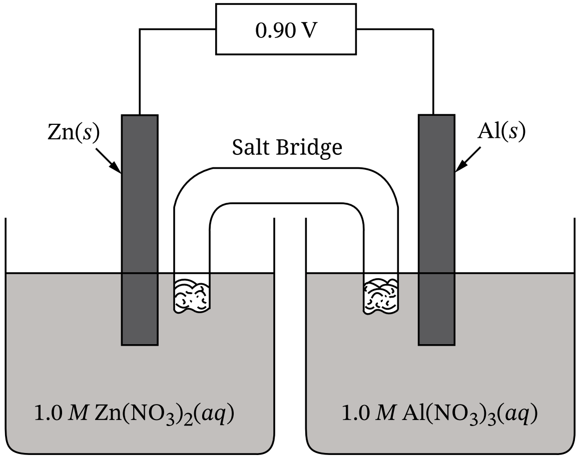
Part F

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)
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	−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)
$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$	+1.50
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$	−0.76
$Mn^{2+}(aq) + 2\ e^- \rightarrow Mn(s)$	−1.19
$Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2\ e^- \rightarrow Be(s)$	−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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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

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.

For each question, show your work for each part in the space provided after that part. 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. Answer the following questions related to manganese compounds.

(a) Manganese has several common oxidation states.

(i) Write the complete electron configuration for an Mn atom in the ground state.

(ii) When manganese forms cations, electrons are lost from which subshell first? Identify both the number and letter associated with the subshell.

A student performs an experiment to produce a manganese salt of unknown composition, $Mn_xCl_y(aq)$, and determine its empirical formula. The student places a sample of $Mn(s)$ in a beaker containing excess $HCl(aq)$, as represented by the following equation.

$$x\ Mn(s) + y\ HCl(aq) \rightarrow Mn_xCl_y(aq) + \frac{y}{2} H_2(g)$$

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.

The student heats the resulting mixture until only $Mn_xCl_y(s)$ remains in the beaker. The data are given in the following table.

Mass of empty beaker	60.169 g
Mass of beaker and Mn(s)	61.262 g
Mass of beaker and Mn_xCl_y after heating to constant mass	62.673 g

(b) Calculate the mass of Cl in the sample of $Mn_xCl_y(s)$ remaining in the beaker.

(c) Calculate the number of moles of Cl in the sample of $Mn_xCl_y(s)$ remaining in the beaker.

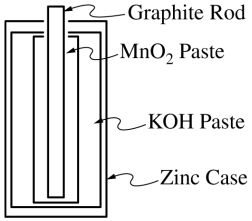
(d) The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the $Mn_xCl_y(s)$.

(e) The student repeats the experiment using the same amounts of Mn and HCl and notices that some of the Mn_xCl_y splatters out of the beaker as it is heated to dryness. Will the number of moles of Cl calculated for this trial be greater than, less than, or equal to the number calculated in part (c) ? Justify your answer.

GO ON TO THE NEXT PAGE.

Continue your response to QUESTION 1 on this page.

(f) Another compound of manganese, MnO_2, is used in alkaline batteries, represented by the following diagram. Some half-reactions are given in the table.



Reduction Half-Reaction	$E°$ (V)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$ZnO(s) + H_2O(l) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$	–1.28
$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$	0.15

(i) Based on the half-reactions given in the table, write the balanced net ionic equation for the reaction that has the greatest thermodynamic favorability.

(ii) Calculate the value of $E°_{cell}$ for the overall reaction.

(iii) Calculate the value of $\Delta G°$ in kJ/mol_{rxn}.

(iv) A student claims that the total mass of an alkaline battery decreases as the battery operates because the anode loses mass. Do you agree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

3. Answer the following questions relating to the element aluminum, Al.

(a) Write the complete ground-state electron configuration of an Al atom.

(b) Based on principles of atomic structure, explain why the radius of the Al atom is larger than the radius of the Al^{3+} ion.

A student plans to combine solid aluminum with an aqueous solution of silver ions. The student determines the mass of solid $AgNO_3$ needed to prepare the solution with a specific concentration.

(c) In the following table, briefly list the steps necessary to prepare 200.0 mL of an aqueous solution of $AgNO_3$ using only equipment selected from the choices given. Assume that all appropriate safety measures are already in place. Not all equipment or lines in the table may be needed.

- Solid $AgNO_3$
- Distilled water
- Balance
- Weighing paper and scoop
- 200.00 mL volumetric flask
- 50.0 mL graduated cylinder
- 250 mL beakers
- Pipet

Step	Step Description
1.	Use weighing paper to measure the determined mass of solid $AgNO_3$ on a balance.
2.	

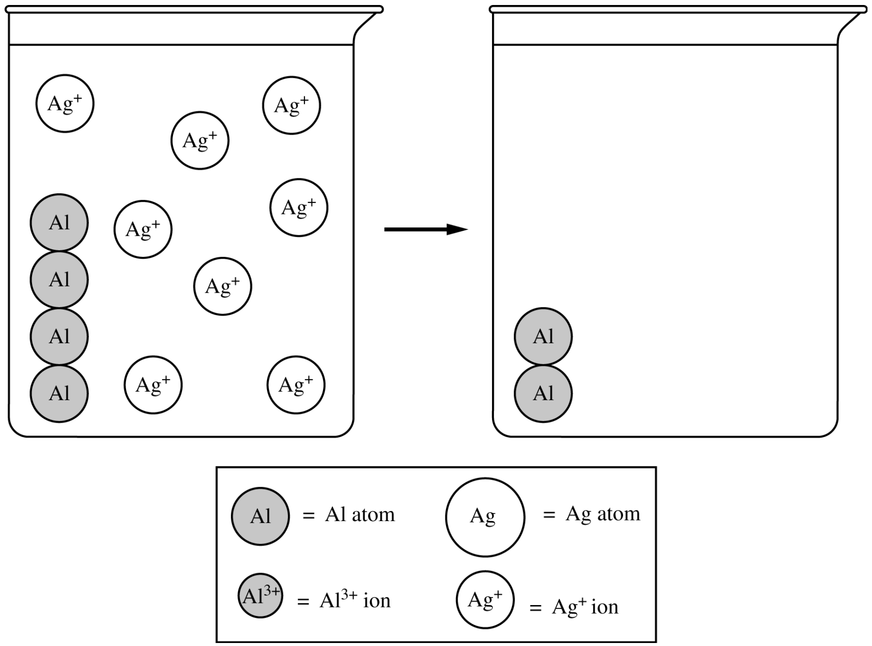
GO ON TO THE NEXT PAGE.

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

After preparing the solution, the student places some of the solution into a beaker and adds a sample of aluminum. The reaction represented by the following equation occurs.

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

(d) The following diagram gives an incomplete particulate representation of the reaction. The beaker on the left represents the system before the mixture reacts. Complete the drawing on the right to represent the system after the reaction has occurred. Be sure to include 1) the correct type and number of particles based on the number shown on the left and 2) the relative spacing to depict the appropriate phases.



The student finds the standard reduction potentials given in the table, which are related to the reaction that occurs.

Half-Reaction	$E°$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	0.80 V
$Al^{3+}(aq) + 3\,e^{-} \rightarrow Al(s)$	−1.66 V

GO ON TO THE NEXT PAGE.

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

(e) Using the standard reduction potentials, calculate the value of $E°$ for the reaction.

(f) Based on the value of $E°$, would the standard free energy change of the reaction under standard conditions, $\Delta G°$, be positive, negative, or zero? Justify your answer.

(g) Once the reaction appears to stop progressing, would the change in free energy, ΔG, be positive, negative, or zero? Justify your answer.

GO ON TO THE NEXT PAGE.

2. Answer the following questions relating to the chemistry of the halogens.

(a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$I_2 + 2e^- \rightarrow 2I^-$	0.53

(b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

Br_2 and Cl_2 can react to form the compound BrCl.

(c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\ \text{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure BrCl(g) is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

(d) Calculate the pressure in the container before equilibrium is established.

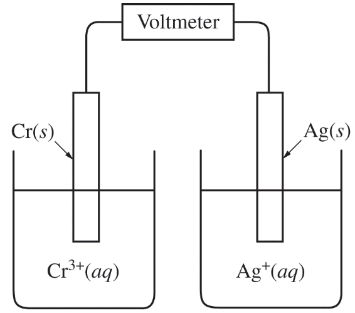
(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of BrCl.

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

(f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.

(g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol_{rxn}) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?



6. A student sets up a galvanic cell at 298 K that has an electrode of Ag(s) immersed in a 1.0 M solution of $Ag^+(aq)$ and an electrode of Cr(s) immersed in a 1.0 M solution of $Cr^{3+}(aq)$, as shown in the diagram above.

(a) The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

Half-Reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	?

(b) The student adds the missing component to the cell and measures $E°_{cell}$ to be +1.54 V. As the cell operates, Ag^+ ions are reduced. Use this information and the information in the table above to do the following.

(i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$.

(ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

(iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol_{rxn}.

7. A student wants to determine the concentration of H_2O_2 in a solution of $H_2O_2(aq)$. The student can use one of two titrants, either dichromate ion, $Cr_2O_7^{2-}(aq)$, or cobalt(II) ion, $Co^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.

Dichromate as titrant: $Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) + 8\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ O_2(g) + 7\ H_2O(l)$

Cobalt(II) as titrant: $2\ Co^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Co^{3+}(aq) + 2\ H_2O(l)$

The half-reactions and the $E°$ values for the systems related to the titrations above are given in the following table.

Half-Reaction	$E°$ (V) at 298 K
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.84
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$	1.77
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.70

(a) Use the information in the table to calculate the following.

(i) $E°$ for the reaction between $Cr_2O_7^{2-}(aq)$ and $H_2O_2(aq)$ at 298 K

(ii) $E°$ for the reaction between $Co^{2+}(aq)$ and $H_2O_2(aq)$ at 298 K

(b) Based on the calculated values of $E°$, the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

(i) Which titrant should the student choose? Explain your reasoning.

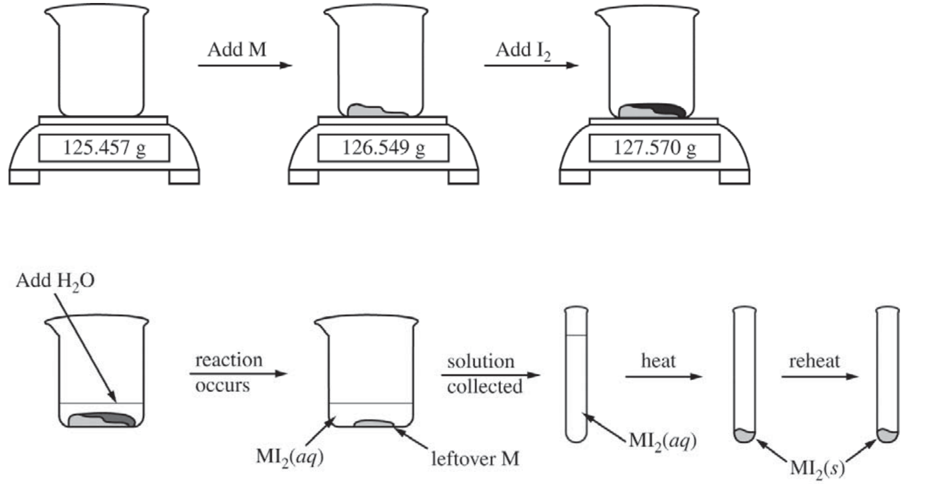
(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction between the chosen titrant and $H_2O_2(aq)$.

STOP

END OF EXAM

$$M + I_2 \rightarrow MI_2$$

3. To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.



Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

(b) Calculate the molar mass of the unknown metal M.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\,e^- \rightarrow 2\,S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer, including a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $\qquad$ $Na_2S_2O_3(aq)$ $\qquad$ $Na_2S_4O_6(aq)$

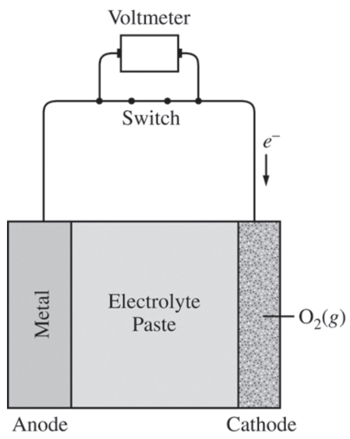
(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

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?