

Question 1

1. A student performs a calorimetry experiment with KCl.

Part A

Consider the K^+ ion in KCl.

- Write** the complete ground-state electron configuration for the potassium ion, K^+ .
- Which has the larger radius, the K^+ ion or the K atom? **Explain** your reasoning using principles of atomic structure.

The following information applies to parts B, C, D, and E.

A student performs an experiment to determine the enthalpy of solution, ΔH_{soln} , of KCl. The student places water in a calorimeter, measures the initial temperature, adds KCl(s), and stirs until the KCl dissolves completely. The temperature is continuously monitored during the experiment. Data from the experiment are given in the following table.

Mass of water	97.5 g
Mass of KCl(s)	6.80 g
Initial temperature of water	24.5°C
Final temperature of solution	21.1°C

Part B

Describe how the student can use the temperature readings during the experiment to determine when the dissolution is complete.

Part C

Use the data in the table to do the following.

- Calculate** the magnitude of the thermal energy, q , in joules, transferred during the dissolution. Show the work that leads to your answer. (Assume that the solution has a specific heat capacity of $3.95 \text{ J/(g}\cdot^\circ\text{C)}$.)
- Calculate** the value of the molar enthalpy of solution, ΔH_{soln} , in kJ/mol, for KCl given that 0.0912 mol of KCl dissolved. Show the work that leads to your answer. Include the sign with your answer.

Part D

The calorimeter is not perfectly insulated. Would this cause the magnitude of ΔH_{soln} calculated in part C (ii) to be greater than, less than, or equal to the accepted value? **Justify** your answer.

Part E

The student performs a second experiment using the same mass of water but 6.80 g of RbCl(s) instead of 6.80 g of KCl(s). The magnitude of the molar enthalpy of solution, ΔH_{soln} , of RbCl is approximately equal to that of KCl.

Is the magnitude of ΔT in the RbCl experiment greater than, less than, or equal to that in the KCl experiment? **Justify** your answer. (Assume that the specific heat capacities of the solutions are equal.)

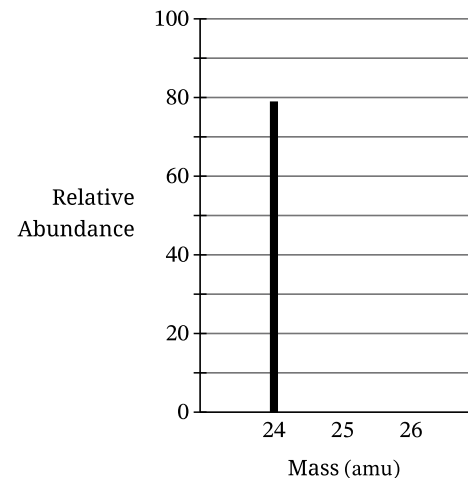
Part F

RbCl has a K_{sp} of 57 at 20°C .

- Write** the net ionic equation for the dissolution of RbCl in pure water.
- Calculate** the molar solubility of RbCl in a saturated solution at 20°C . Show the work that leads to your answer.
- A second saturated solution is prepared by dissolving RbCl(s) in 1.0 M KCl(aq) at 20°C instead of in pure water. Will the molar solubility of RbCl in 1.0 M KCl(aq) be greater than, less than, or equal to the molar solubility calculated in part F (ii)? **Justify** your answer.

1. Answer the following questions about magnesium.

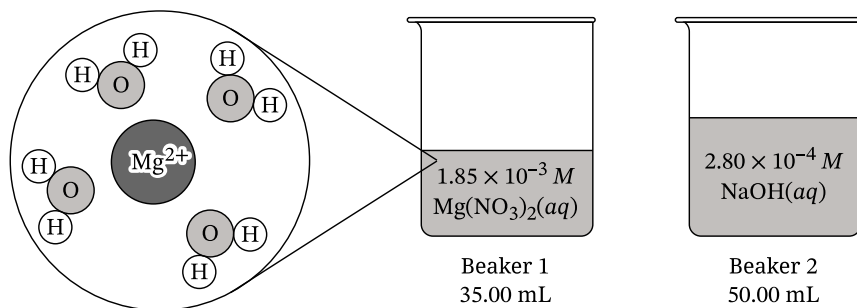
A. An incomplete mass spectrum for magnesium is shown in the diagram.



The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

- Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.
- Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a $1.85 \times 10^{-3} M$ solution of $\text{Mg}(\text{NO}_3)_2(aq)$ in beaker 1 and a $2.80 \times 10^{-4} M$ solution of $\text{NaOH}(aq)$ in beaker 2, as shown.

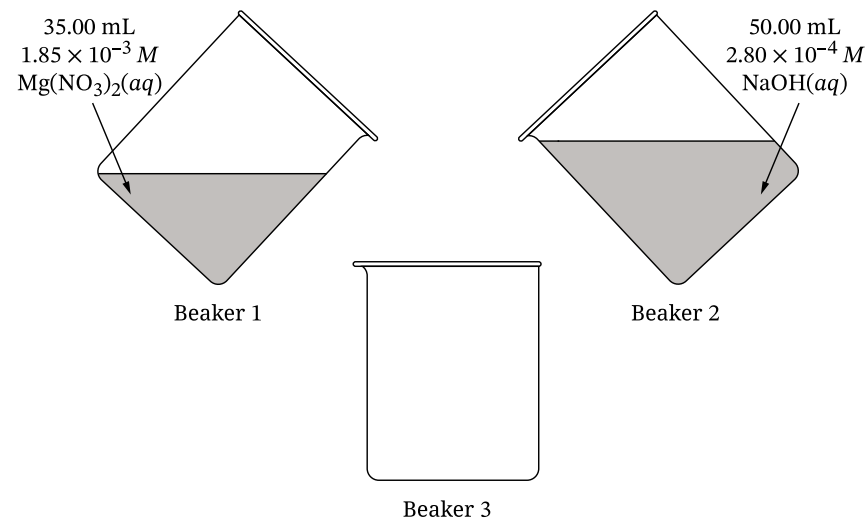


B. The particle diagram shown represents a magnesium ion, Mg^{2+} , in beaker 1. A sodium ion, Na^+ , in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

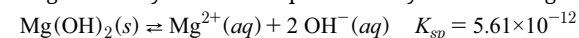
- The relative charge of the ions
- The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

D. A student combines 35.00 mL of $1.85 \times 10^{-3} M \text{Mg}(\text{NO}_3)_2(aq)$ with 50.00 mL of $2.80 \times 10^{-4} M \text{NaOH}(aq)$, as shown in the diagram. Calculate $[\text{Mg}^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



E. The dissolution of magnesium hydroxide is represented by the following equation.



- Write the expression for the solubility product constant, K_{sp} .
 - After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[\text{OH}^-] = 1.65 \times 10^{-4} M$. Using your answer to part D, calculate the value of the reaction quotient, Q .
 - Using the reaction quotient, Q , predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.
- F. In a separate experiment, the student adds $\text{HNO}_3(aq)$ to decrease the pH of a saturated solution containing undissolved $\text{Mg}(\text{OH})_2(s)$. Does the amount of undissolved $\text{Mg}(\text{OH})_2(s)$ increase, decrease, or remain the same as the $\text{HNO}_3(aq)$ is added? Justify your answer.

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.

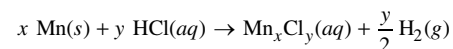
1. Answer the following questions related to manganese compounds.

(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, $\text{Mn}_x\text{Cl}_y(\text{aq})$, and determine its empirical formula. The student places a sample of $\text{Mn}(\text{s})$ in a beaker containing excess $\text{HCl}(\text{aq})$, as represented by the following equation.



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

The student heats the resulting mixture until only $\text{Mn}_x\text{Cl}_y(\text{s})$ remains in the beaker. The data are given in the following table.

Mass of empty beaker	60.169 g
Mass of beaker and $\text{Mn}(\text{s})$	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 $\text{Mn}_x\text{Cl}_y(\text{s})$ remaining in the beaker.

(c) Calculate the number of moles of Cl in the sample of $\text{Mn}_x\text{Cl}_y(\text{s})$ remaining in the beaker.

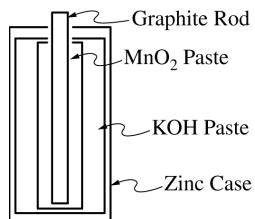
(d) The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the $\text{Mn}_x\text{Cl}_y(\text{s})$.

(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.

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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)
$\text{Zn}^{2+}(aq) + 2 e^- \rightarrow \text{Zn}(s)$	-0.76
$\text{ZnO}(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Zn}(s) + 2 \text{OH}^-(aq)$	-1.28
$2 \text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2 \text{OH}^-(aq)$	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 ΔG° in $\text{kJ/mol}_{\text{rxn}}$.

- (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.

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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.

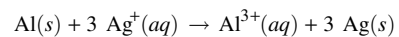
- | | | |
|-------------------------|------------------------------|------------------|
| · Solid AgNO_3 | · Weighing paper and scoop | · 250 mL beakers |
| · Distilled water | · 200.00 mL volumetric flask | · Pipet |
| · Balance | · 50.0 mL graduated cylinder | |

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

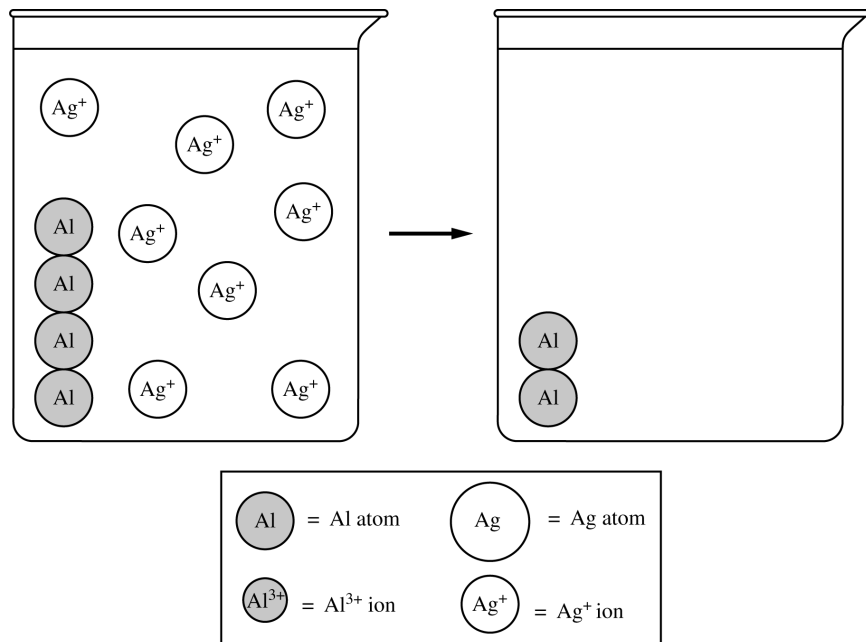
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Continue your response to **QUESTION 2** on this page.

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.



- (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°
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	0.80 V
$\text{Al}^{3+}(aq) + 3 e^- \rightarrow \text{Al}(s)$	-1.66 V

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

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

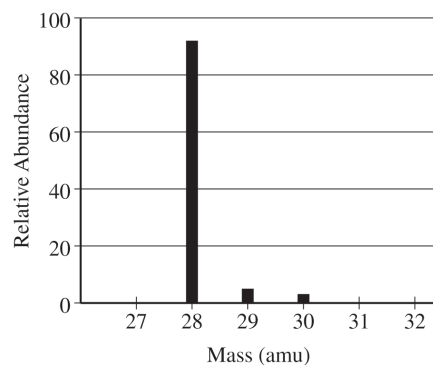
- (f) Based on the value of E° , would the standard free energy change of the reaction under standard conditions, ΔG° , be positive, negative, or zero? Justify your answer.

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

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1. Answer the following questions about the element Si and some of its compounds.

(a) The mass spectrum of a pure sample of Si is shown below.



(i) How many protons and how many neutrons are in the nucleus of an atom of the most abundant isotope of Si?

(ii) Write the ground-state electron configuration of Si.

Two compounds that contain Si are SiO_2 and SiH_4 .

(b) At 161 K, SiH_4 boils but SiO_2 remains as a solid. Using principles of interparticle forces, explain the difference in boiling points.

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

At high temperatures, SiH_4 decomposes to form solid silicon and hydrogen gas.

(c) Write a balanced equation for the reaction.

A table of absolute entropies of some substances is given below.

Substance	S° (J/(mol · K))
$\text{H}_2(g)$	131
$\text{Si}(s)$	18
$\text{SiH}_4(g)$	205

(d) Explain why the absolute molar entropy of $\text{Si}(s)$ is less than that of $\text{H}_2(g)$.

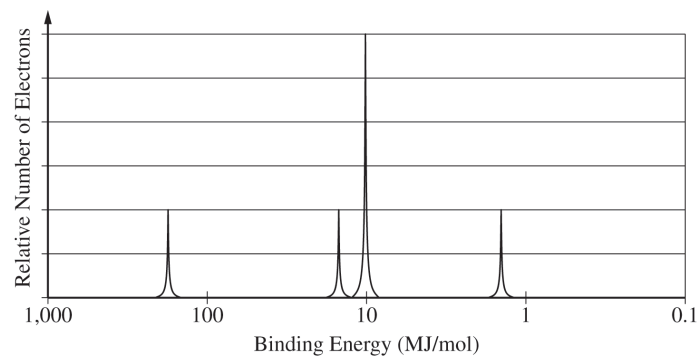
(e) Calculate the value, in J/(mol · K), of ΔS° for the reaction.

(f) The reaction is thermodynamically favorable at all temperatures. Explain why the reaction occurs only at high temperatures.

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(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the $3p$ sublevel.



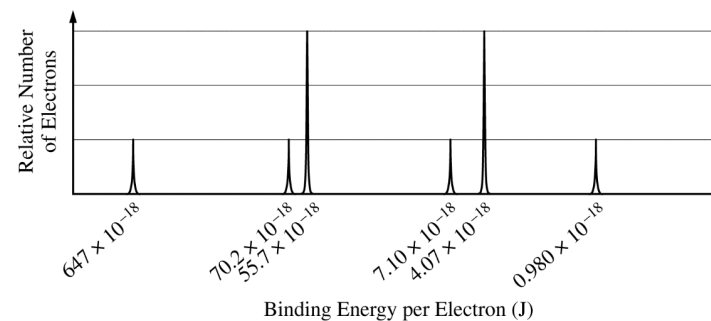
(h) Using principles of atomic structure, explain why the first ionization energy of Ge is lower than that of Si.

(i) A single photon with a wavelength of $4.00 \times 10^{-7} \text{ m}$ is absorbed by the Si sample. Calculate the energy of the photon in joules.

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Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

5. The complete photoelectron spectrum of an element in its ground state is represented below.



- (a) Based on the spectrum,
- write the ground-state electron configuration of the element, and
 - identify the element.
- (b) Calculate the wavelength, in meters, of electromagnetic radiation needed to remove an electron from the valence shell of an atom of the element.

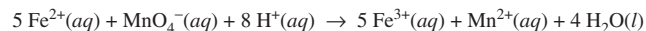
3. Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+} .

- (a) Write the ground-state electron configuration of the Fe^{2+} ion.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

- (b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.
- (c) Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

A student obtains a solution that contains an unknown concentration of $\text{Fe}^{2+}(aq)$. To determine the concentration of $\text{Fe}^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $\text{MnO}_4^-(aq)$, which converts $\text{Fe}^{2+}(aq)$ to $\text{Fe}^{3+}(aq)$, as represented by the following equation.



- (d) Write the balanced equation for the half-reaction for the oxidation of $\text{Fe}^{2+}(aq)$ to $\text{Fe}^{3+}(aq)$.
- (e) The student titrates a 10.0 mL sample of the $\text{Fe}^{2+}(aq)$ solution. Calculate the value of $[\text{Fe}^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $\text{KMnO}_4(aq)$ to reach the equivalence point of the titration.

To deliver the 10.0 mL sample of the $\text{Fe}^{2+}(aq)$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

- (f) Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $\text{Fe}^{2+}(aq)$ solution.

In a separate experiment, the student is given a sample of powdered $\text{Fe}(s)$ that contains an inert impurity. The student uses a procedure to oxidize the $\text{Fe}(s)$ in the sample to $\text{Fe}_2\text{O}_3(s)$. The student collects the following data during the experiment.

Mass of $\text{Fe}(s)$ with inert impurity	6.724 g
Mass of $\text{Fe}_2\text{O}_3(s)$ produced	7.531 g

- (g) Calculate the number of moles of Fe in the $\text{Fe}_2\text{O}_3(s)$ produced.
- (h) Calculate the percent by mass of Fe in the original sample of powdered $\text{Fe}(s)$ with the inert impurity.
- (i) If the oxidation of the $\text{Fe}(s)$ in the original sample was incomplete so that some of the 7.531 g of product was $\text{FeO}(s)$ instead of $\text{Fe}_2\text{O}_3(s)$, would the calculated mass percent of $\text{Fe}(s)$ in the original sample be higher, lower, or the same as the actual mass percent of $\text{Fe}(s)$? Justify your answer.

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.

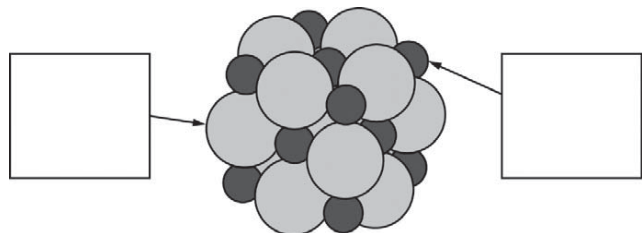
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer.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

1. A student investigates the enthalpy of solution, ΔH_{soln} , for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of ± 0.1 g, and a thermometer with a precision of $\pm 0.1^\circ\text{C}$.
- (a) To measure ΔH_{soln} for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl(s), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C .
- (i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is $4.18 \text{ J/(g}\cdot^\circ\text{C)}$. Include units with your answer.
- (ii) Determine the value of ΔH_{soln} for LiCl in $\text{kJ/mol}_{\text{rxn}}$.

To explain why ΔH_{soln} for NaCl is different than that for LiCl, the student investigates factors that affect ΔH_{soln} and finds that ionic radius and lattice enthalpy (which can be defined as the ΔH associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

Ion	Ionic Radius (pm)
Li^+	76
Na^+	102

- (b) Write the complete electron configuration for the Na^+ ion in the ground state.
- (c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.
- (d) Which salt, LiCl or NaCl , has the greater lattice enthalpy? Justify your answer.
- (e) Below is a representation of a portion of a crystal of LiCl . Identify the ions in the representation by writing the appropriate formulas (Li^+ or Cl^-) in the boxes below.

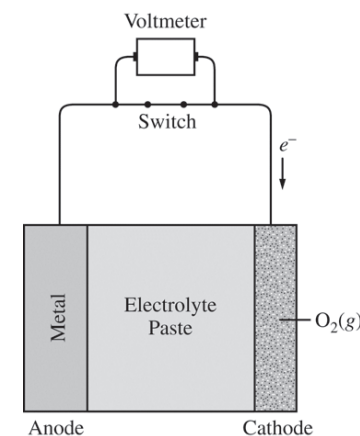


- (f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl . However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

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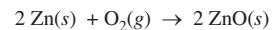
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. 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)
$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 e^- \rightarrow 4 \text{OH}^-(aq)$	+0.34
$\text{ZnO}(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Zn}(s) + 2 \text{OH}^-(aq)$	−1.31
$\text{Na}_2\text{O}(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow 2 \text{Na}(s) + 2 \text{OH}^-(aq)$	−1.60
$\text{CaO}(s) + \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{Ca}(s) + 2 \text{OH}^-(aq)$	−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.



- (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?