Question 1

1. A student performs a calorimetry experiment with KCl.

Part A

Consider the K^+ ion in KCl.

i. **Write** the complete ground-state electron configuration for the potassium ion, K^+.

ii. 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.

i. **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 $3.95\ J/(g{\cdot}°C)$.)

ii. **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.

i. **Write** the net ionic equation for the dissolution of RbCl in pure water.

ii. **Calculate** the molar solubility of RbCl in a saturated solution at 20°C. Show the work that leads to your answer.

iii. 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.

Question 7

The following information applies to parts A and B.

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7. Sodium metal reacts with oxygen gas according to Equation 1.

$$\text{Equation 1: } 4\ Na(s) + O_2(g) \rightarrow 2\ Na_2O(s) \qquad \Delta H^\circ_{rxn} = -828\ \text{kJ/mol}_{rxn}$$

Standard enthalpies of formation are provided in Table 1.

Table 1

Substance	ΔH°_f (kJ/mol)
$Na(s)$	0
$O_2(g)$	0
$Na_2O(s)$	?

Part A

Based on the information given, **calculate** the value of ΔH°_f for $Na_2O(s)$. Show the work that leads to your answer.

Part B

An 18.4 g sample of $Na(s)$ reacts with 12.8 g of $O_2(g)$ according to Equation 1. **Calculate** the total amount of heat, in kilojoules, released during this process. Show the work that leads to your answer.

Part C

Lattice enthalpy can be defined as the energy required to separate an ionic crystal into gaseous ions. $Rb_2O\,(s)$ and $Na_2O\,(s)$ have similar crystal structures, and their lattice enthalpies are given in Table 2.

Table 2

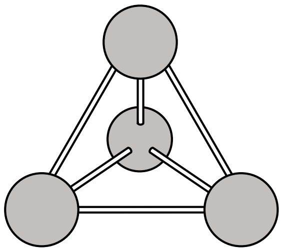
Compound	Lattice Enthalpy (kJ/mol)
$Na_2O\,(s)$	2481
$Rb_2O\,(s)$	2163

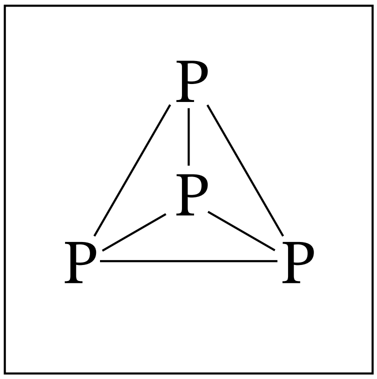
Using Coulomb's law, **explain** why the lattice enthalpy of $Rb_2O\,(s)$ is smaller than that of $Na_2O\,(s)$.

STOP

END OF EXAM

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.





A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.

B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

$$\text{Equation 1: } P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$$

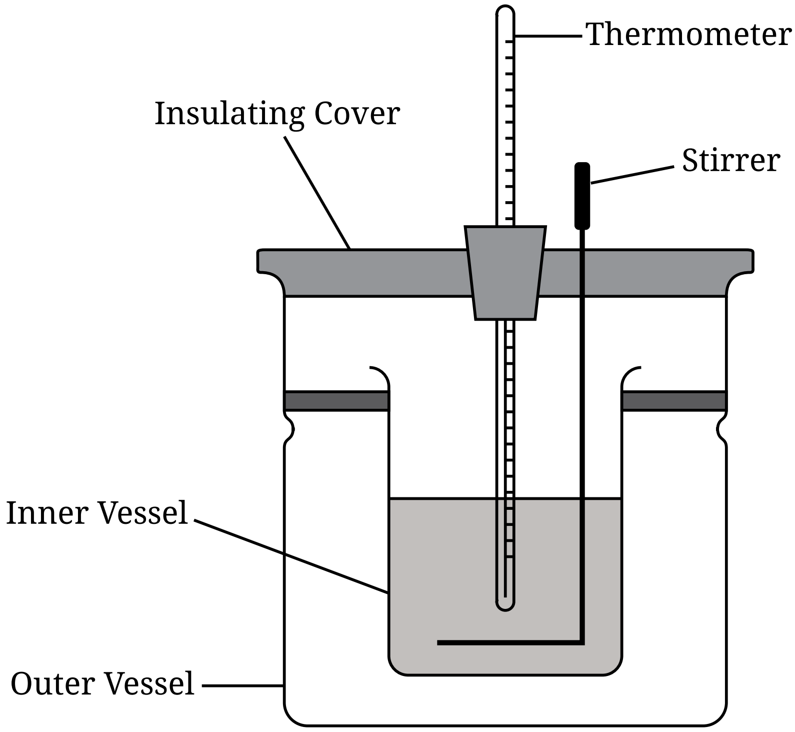
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

ii. The enthalpy change of the reaction, ΔH°, is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG°, ΔH°, and ΔS°.

$P_4O_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.

$$\text{Equation 2: } P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$$

A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

i. Calculate the amount of heat, q, released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.

ii. Calculate the value of ΔH°_{rxn} for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

$P_4(s)$ also reacts readily with $Cl_2(g)$ to produce phosphorus trichloride, $PCl_3(g)$, which in turn reacts with $Cl_2(g)$ in an equilibrium process to produce $PCl_5(g)$. The reactions are represented by equations 3 and 4.

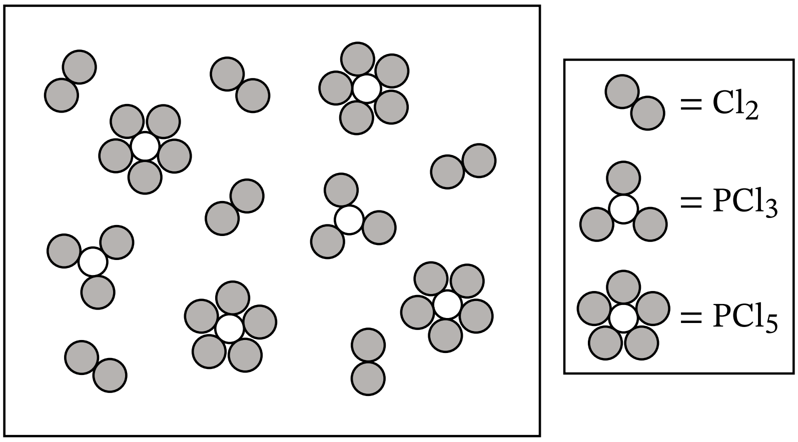
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

E. Calculate the standard enthalpy of formation of $PCl_5(g)$ represented by equation 5.

$$\text{Equation 5: } \frac{1}{4}P_4(s) + \frac{5}{2}Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H_f^\circ = ?$$

The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



F. Equation 4 for the reaction that occurs is shown.

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

i. If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?

ii. Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2°.

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

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

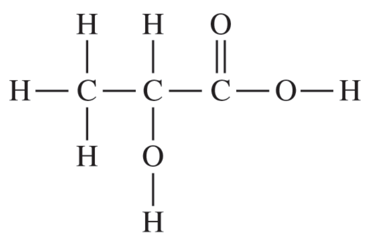
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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.

$$C_3H_6O_3(aq) + NaOH(aq) \rightarrow NaC_3H_5O_3(aq) + H_2O(l)$$

1. A student is studying the reaction between lactic acid, $C_3H_6O_3$, and sodium hydroxide, NaOH, as represented in the balanced equation above.

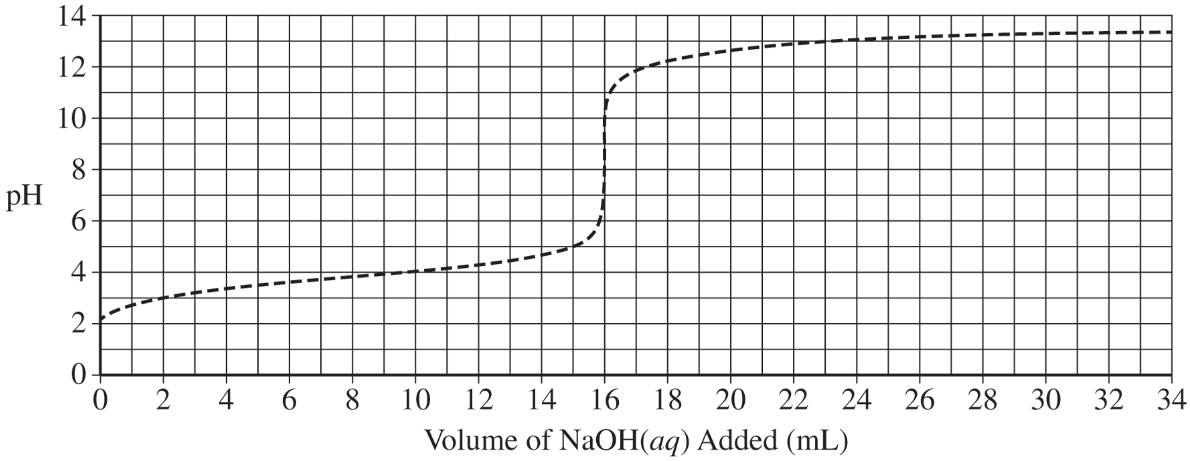
(a) The structural formula of lactic acid is shown in the following diagram. Circle the hydrogen atom that most readily participates in the chemical reaction with sodium hydroxide.



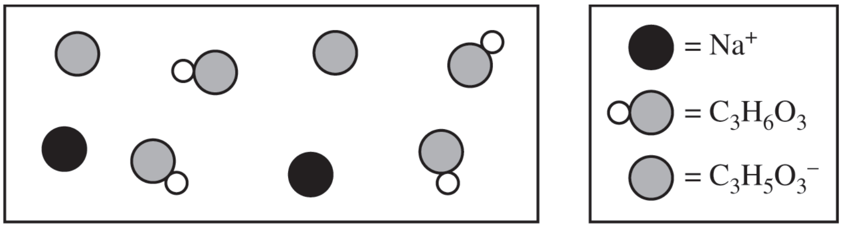
(b) The student begins the experiment by dissolving 10.22 g of sodium hydroxide (molar mass 40.00 g / mol) in enough water to produce 500. mL of solution. Calculate the molarity of the sodium hydroxide solution.

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

The student uses the sodium hydroxide solution from part (b), a buret, a pH meter, and a 100 mL Erlenmeyer flask to titrate a 25.0 mL sample of lactic acid solution. The student's data are shown in the following graph.



(c) Use the information in the graph to determine the approximate pK_a of lactic acid. ____________



(d) The preceding diagram represents the relative amounts of major species in a sample of the solution in the flask at one point during the titration. (Note that water molecules are omitted.)

(i) Draw an X on the preceding titration curve at a point in the titration where the reaction mixture would be represented by this diagram.

(ii) Justify your answer.

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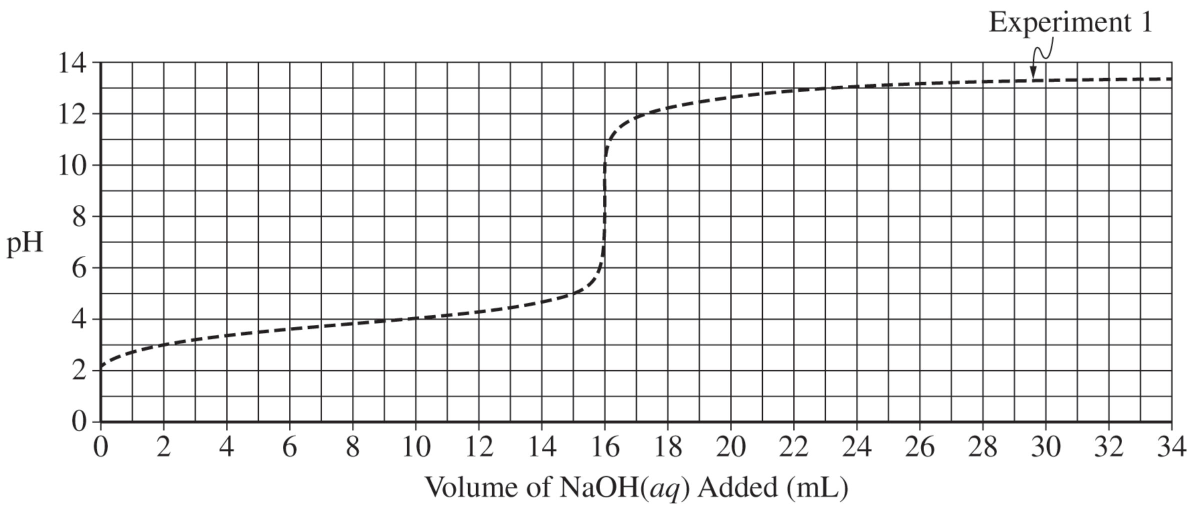
Continue your response to **QUESTION 1** on this page.

Experiment	Mass of $NaOH(s)$ (grams)	Volume of Solution (mL)	Titration Curve
1	10.22	500.	Already shown on graph
2	20.44	500.	?

(iii) The student repeats the experiment but uses a solution of $NaOH(aq)$ with twice the concentration, as shown in the preceding table. On the following graph, draw the titration curve that would be expected for experiment 2.



(e) In a third experiment, the student investigates the enthalpy of the reaction between lactic acid and sodium hydroxide. The student combines 100.0 mL of a 0.500 M lactic acid solution at 20.0°C with 100.0 mL of a 0.500 M NaOH solution at 20.0°C in a calorimeter. The final temperature of the resulting combined solution is 23.2°C. Assume that the density of each solution before combining is 1.00 g / mL and that the specific heat capacity of the combined solution is 4.2 J / (g · °C).

(i) Calculate the quantity of heat produced in the reaction, in J.

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

(ii) Calculate the molar enthalpy of reaction, in kJ / mol_{rxn}. Include the sign in your answer.

(iii) The student claims that if heat is lost from the calorimeter to the surrounding air during the reaction, then the experimental value of the molar enthalpy of reaction will be smaller in magnitude than the actual value. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

. Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

(a) Write the balanced net ionic equation for the reaction.

A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $HCl(aq)$ at 21.2° C with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

Trial	Concentration of $HCl(aq)$ (M)	Particle Size of $CaCO_3(s)$	Time of Reaction (s)
1	1.00	Fine powder	67
2	1.00	Small chunks	112
3	1.00	Large chunk	342
4	3.00	Fine powder	22
5	3.00	Small chunks	227
6	3.00	Large chunk	114

(b) The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

GO ON TO THE NEXT PAGE.

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

(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

(d) The student claims that the reaction is zero order with respect to $HCl(aq)$. Do you agree or disagree with the student's claim? Justify your answer using the student's data.

(e) The $HCl(aq)$ was present in excess in all trials of the experiment. Determine the molarity of the $HCl(aq)$ in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of $CaCO_3$ is 100.09 g/mol.)

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Continue your response to **QUESTION [illegible]** on this page.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Time (s)	Measured Temperature of Solution (°C)
0	21.20
20	21.51
40	21.70
60	21.85
80	21.90
100	21.90

(f) Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

GO ON TO THE NEXT PAGE.

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

(g) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is $4.0\ \text{J}/(\text{g} \cdot {}^\circ\text{C})$.

(i) Calculate the magnitude of heat transfer, q, in joules.

(ii) Calculate the enthalpy of reaction in units of kJ/mol_{rxn}. Include the algebraic sign on your answer.

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CHEMISTRY

Section II

Time—1 hour and 45 minutes

7 Questions

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.

$$Na_2S_2O_3(aq) + 4\ NaOCl(aq) + 2\ NaOH(aq) \rightarrow 2\ Na_2SO_4(aq) + 4\ NaCl(aq) + H_2O(l)$$

1. A student performs an experiment to determine the value of the enthalpy change, ΔH°_{rxn}, for the oxidation-reduction reaction represented by the balanced equation above.

(a) Determine the oxidation number of Cl in NaOCl.

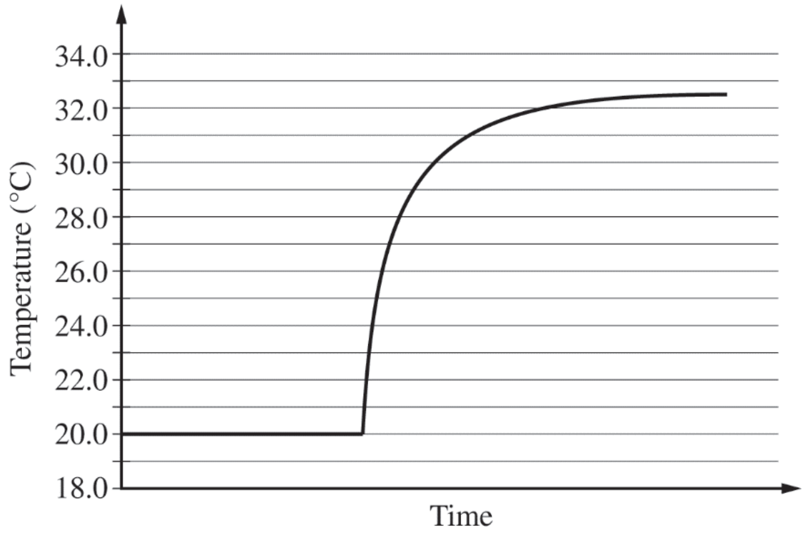
(b) Calculate the number of grams of $Na_2S_2O_3$ needed to prepare 100.00 mL of 0.500 M $Na_2S_2O_3(aq)$.

In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5.00
$NaOCl(aq)$	0.500	5.00
$NaOH(aq)$	0.500	5.00

(c) Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture?

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, ΔH°_{rxn}, in kJ/mol_{rxn}. Include the appropriate algebraic sign with your answer.

The student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration (M)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	10.0
$NaOCl(aq)$	0.500	10.0
$NaOH(aq)$	0.500	10.0

(f) The magnitude of the enthalpy change, ΔH°_{rxn}, in kJ/mol_{rxn}, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

(g) Write the balanced net ionic equation for the given reaction.