Question 1

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

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.

+1	1 point is earned for the correct answer.

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

$100.00\text{ mL} \times \frac{0.500\text{ mol } Na_2S_2O_3}{1000\text{ mL}} \times \frac{158.10\text{ g } Na_2S_2O_3}{1\text{ mol } Na_2S_2O_3}$ $= 7.90\text{ g } Na_2S_2O_3$	1 point is earned for the correct number of moles of $Na_2S_2O_3$ (may be implicit). 1 point is earned for the correct calculation of mass of $Na_2S_2O_3$ consistent with the number of moles.

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

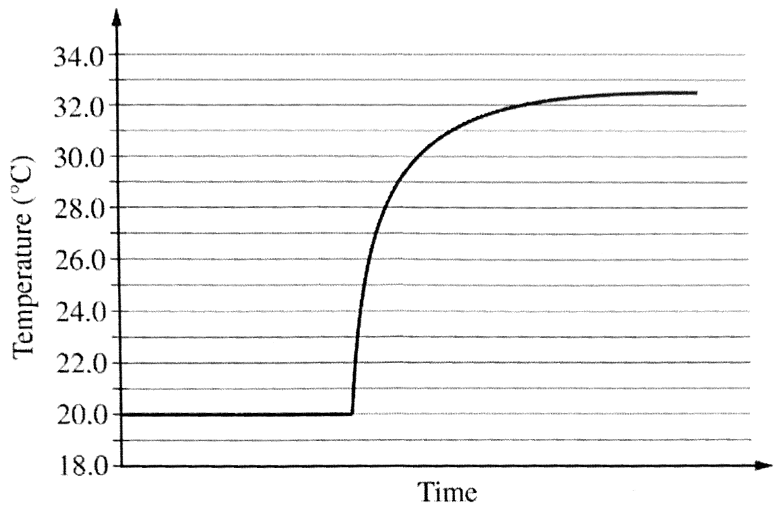
Solution	Concentration (*M*)	Volume (mL)
$Na_2S_2O_3(aq)$	0.500	5.00
$NaOCl(aq)$	0.500	5.00
$NaOH(aq)$	0.500	5.00

(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.

NaOCl is the limiting reactant. Given that equal numbers of moles of each reactant were present initially, it follows from the coefficients of the reactants in the balanced equation that NaOCl will be depleted first.	1 point is earned for identifying the limiting reactant <u>and</u> providing a valid justification.

Question 1 (continued)

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?

From the graph the final temperature is 32.5°C. $\Delta T = T_f - T_i = 32.5°C - 20.0°C = 12.5°C$	1 point is earned for the correct value of ΔT.

(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.

$q = mc\Delta T$ $= (15.21 \text{ g})(3.94 \text{ J/(g·°C)})(12.5°C) = 749 \text{ J}$	1 point is earned for the correct calculation of q consistent with the ΔT value from part (d).

(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.

Question 1 (continued)

$n_{NaOCl} = 5.00 \text{ mL} \times \dfrac{0.500 \text{ mol NaOCl}}{1000 \text{ mL NaOCl}} = 0.00250 \text{ mol NaOCl}$ $n_{rxn} = 0.00250 \text{ mol NaOCl} \times \dfrac{1 \text{ mol}_{rxn}}{4 \text{ mol NaOCl}} = 0.000625 \text{ mol}_{rxn}$ $\Delta H^\circ_{rxn} = \dfrac{-0.749 \text{ kJ}}{0.000625 \text{ mol}_{rxn}} = -1.20 \times 10^3 \text{ kJ/mol}_{rxn}$	1 point is earned for correctly calculating the value of mol_{rxn} consistent with the limiting reactant in part (c). 1 point is earned for a negative ΔH°_{rxn} obtained by dividing the calculated value of q by the calculated value of mol_{rxn}.

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.

By doubling the volumes, the number of moles of the reactants are doubled, which doubles the amount of energy produced. Therefore the amount of heat per mole will remain the same. OR In the second experiment, $\Delta H^\circ_{rxn} = \dfrac{2mc\Delta T}{2n} = \dfrac{mc\Delta T}{n} = \Delta H^\circ_{rxn}$. Thus the magnitude is the same as calculated in the first experiment.	1 point is earned for a valid explanation.

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

$S_2O_3^{2-}(aq) + 4\ OCl^-(aq) + 2\ OH^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + 4\ Cl^-(aq) + H_2O(l)$	1 point is earned for the correct net ionic equation.

Question 2

Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.

$$\mathrm{H{-}C{\equiv}N{-}\ddot{\underset{\cdot\cdot}{O}}\!:} \qquad\qquad \mathrm{H{-}\ddot{C}{=}N{=}\ddot{O}\!:}$$

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of −1. In the diagram on the right, the C atom has a formal charge of −1 and the O atom has a formal charge of zero.	1 point is earned for a correct assignment of formal charges in the two diagrams.
The diagram on the left is the better representation because it puts the negative formal charge on oxygen, which is more electronegative than carbon.	1 point is earned for a correct explanation.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$\mathrm{HCNO}(g) \rightleftarrows \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
$\mathrm{H{-}C{\equiv}N{-}\ddot{\underset{\cdot\cdot}{O}}\!:}$	$\mathrm{H{-}\ddot{N}{=}C{=}\ddot{O}\!:}$

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of $\mathrm{HCNO}(g)$ to form $\mathrm{HNCO}(g)$.

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N−O	201	C=N	615	H−C	413
C=O	745	C≡N	891	H−N	391

Compound	HCNO	HNCO
Bond Enthalpies (kJ/mol)	413 + 891 + 201	391 + 615 + 745
Total Bond Enthalpy (kJ/mol)	1505	1751

$$\Delta H° = \Sigma(\text{enthalpies of bonds broken}) - \Sigma(\text{enthalpies of bonds formed})$$
$$= 1505 \text{ kJ/mol} - 1751 \text{ kJ/mol}$$
$$= -246 \text{ kJ/mol}_{rxn}$$

1 point is earned for subtracting the enthalpies of bonds formed from the enthalpies of bonds broken.

1 point is earned for the correct determination of $\Delta H°$.

Question 2 (continued)

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

The change from fulminic acid to isocyanic acid is a rearrangement of atoms with no change in phase or number of molecules.	1 point is earned for a correct explanation.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

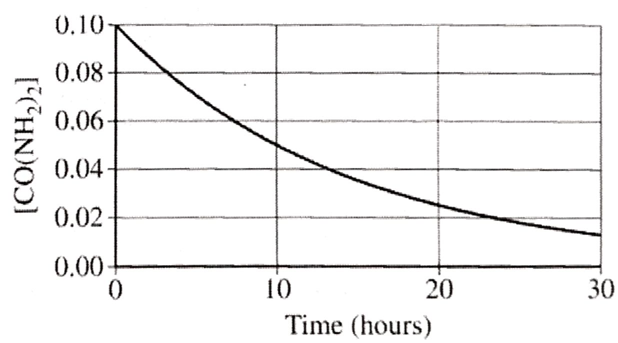
Isocyanic acid (HNCO) will be present in higher concentration. $\Delta G°$ is essentially equal to $\Delta H°$ because $\Delta S°$ is essentially zero, so $\Delta G° \approx -246$ kJ/mol_{rxn}, indicating the forward reaction is thermodynamically favorable.	1 point is earned for the correct choice **with** a valid justification. (Calculation of $\Delta G°$ is a sufficient justification.)
Since $\Delta G°$ is negative, $K > 1$ ($\Delta G° = -RT \ln K$), resulting in a higher concentration of product than reactant at equilibrium.	1 point is earned for correctly connecting thermodynamic favorability to the equilibrium constant, K.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

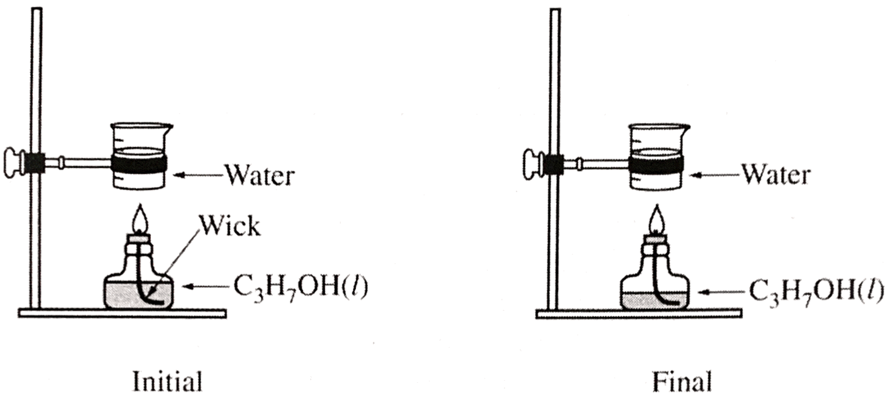
Time (hours)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



Question 5

$$2\ C_3H_7OH(l) + 9\ O_2(g) \rightarrow 6\ CO_2(g) + 8\ H_2O(g)$$

A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH(l)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $C_3H_7OH(l)$ that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH(l)$ combusted is determined by weighing the alcohol burner before and after combustion.



Data from the experiment are given in the table below.

Mass of $C_3H_7OH(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	22.0°C
Final temperature of water	51.1°C
Specific heat of water	4.18 J/(g·°C)

(a) Calculate the magnitude of the heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)

$q = mc\Delta T$ $= (125.00\text{ g})(4.18\text{ J/(g·°C)})(51.1°\text{C} - 22.0°\text{C})$ $= 15{,}200\text{ J} = 15.2\text{ kJ}$	1 point is earned for the correct calculation.

Question 5 (continued)

(b) Based on the experimental data, if one mole of $C_3H_7OH(l)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.

$1 \text{ mol } C_3H_7OH \times \frac{60.09 \text{ g } C_3H_7OH}{1 \text{ mol } C_3H_7OH} \times \frac{15.2 \text{ kJ}}{0.55 \text{ g } C_3H_7OH} = 1661 \text{ kJ}$ $= 1.7 \times 10^3 \text{ kJ}$	1 point is earned for the correct amount of heat released. 1 point is earned for reporting the answer to the appropriate number of significant figures based on the experimental data.

(c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $C_3H_7OH(l)$ that is contaminated with water, which is miscible with $C_3H_7OH(l)$. The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

The final temperature measured by the second student would be less than that measured by the first student because: the actual mass of $C_3H_7OH(l)$ combusted will be less than 0.55 g OR combustion of the contaminated sample will also require vaporization of the water in the sample.	1 point is earned for the correct choice **with** a valid explanation.

Question 2

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

It is an acid-base reaction. The weak acid $HC_2H_3O_2$ reacts with the weak base HCO_3^- with $HC_2H_3O_2$ donating a proton. OR It is an acid-base reaction. No solid precipitates, so it is not a precipitation reaction. None of the oxidation numbers change, so it is not a redox reaction.	1 point is earned for identifying the reaction as acid-base. 1 point is earned for the justification.

(b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

$2.24 \text{ g } NaHCO_3 \times \frac{1 \text{ mol } NaHCO_3}{84.0 \text{ g}} = 0.0267 \text{ mol } NaHCO_3$ $60.0 \text{ mL} \times \frac{0.875 \text{ mol } HC_2H_3O_2}{1000 \text{ mL}} = 0.0525 \text{ mol } HC_2H_3O_2$ The $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$ react in a 1:1 ratio, so the limiting reactant is $NaHCO_3(s)$.	1 point is earned for calculating the number of moles of each reactant. 1 point is earned for identifying the limiting reactant consistent with the calculations.

(c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

As the reaction proceeds, both reactants are consumed and their concentrations decrease. Collisions between reactant particles become less likely as their concentations decrease, thus the reaction rate slows.	1 point is earned for a valid explanation.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only   Entropy only   Both enthalpy and entropy

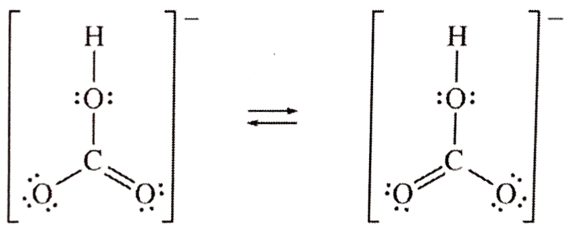
Entropy only should be circled.	1 point is earned for circling Entropy only.

Question 2 (continued)

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

$\Delta G° = \Delta H° - T\Delta S°$ Reactions are thermodynamically favorable when $\Delta G°$ is negative. Since the reaction is endothermic (the flask gets cooler, $\Delta H°$ is positive), the reaction is not driven by enthalpy, because enthalpy does not help make $\Delta G°$ negative. Because there are no gases in the reactants and one of the products is a gas, $\Delta S°$ must be positive, which helps make $\Delta G°$ negative.	1 point is earned for a valid justification.

(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.



See diagram above.	1 point is earned for a correct Lewis structure of HCO_3^-. 1 point is earned for indicating resonance (e.g., two diagrams, or one diagram with an arrow between the two appropriate oxygen atoms).

(f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 *M* $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.

$C_2H_3O_2^- + H_3O^+ \rightarrow HC_2H_3O_2 + H_2O$ OR $C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$	1 point is earned for a correct equation.

Question 6 (continued)

In a separate experiment, the student measures the enthalpies of combustion of propene and vinyl chloride. The student determines that the combustion of 2.00 mol of vinyl chloride releases 2300 kJ of energy, according to the equation below.

$$2\ C_2H_3Cl(g)\ +\ 5\ O_2(g) \rightarrow 4\ CO_2(g)\ +\ 2\ H_2O(g)\ +\ 2\ HCl(g) \qquad \Delta H° = -2300\ \text{kJ/mol}_{rxn}$$

(c) Using the table of standard enthalpies of formation below, determine whether the combustion of 2.00 mol of propene releases more, less, or the same amount of energy that 2.00 mol of vinyl chloride releases. Justify your answer with a calculation. The balanced equation for the combustion of 2.00 mol of propene is $2\ C_3H_6(g)\ +\ 9\ O_2(g) \rightarrow 6\ CO_2(g)\ +\ 6\ H_2O(g)$.

Substance	$C_2H_3Cl(g)$	$C_3H_6(g)$	$CO_2(g)$	$H_2O(g)$	$HCl(g)$	$O_2(g)$
Standard Enthalpy of Formation (kJ/mol)	37	21	−394	−242	−92	0

$\Delta H° = 6(-394) + 6(-242) - 2(21) = -3858\ \text{kJ/mol}_{rxn}$	1 point is earned for the calculation of the enthalpy of combustion of propene.
The combustion of 2.00 mol of propene releases more energy.	1 point is earned for the comparison of propene to vinyl chloride that is consistent with the calculated value.