Practice Problems: Thermodynamics

1. Answer the questions below for each of the following reaction coordinate diagrams:

   ![Reaction Coordinate Diagrams]

   a) Is the reaction exothermic or endothermic?

      **exothermic**  **endothermic**

   b) What is the sign of $\Delta H$?

      $(-)$  $(+)$

   c) Is heat absorbed or released?

      released  absorbed

   d) What happens to the temperature of the surroundings?

      increases (gets warmer)  decreases (gets colder)

   e) What does the asterisk ($\ast$) at the top of the hill represent?

      **activated complex**  **high energy transition state**

2. Based on the following equation:

   \[
   2 \text{ C}_3\text{H}_7\text{OH} \,(l) + 9 \text{ O}_2 \,(g) \rightarrow 6 \text{ CO}_2 \,(g) + 8 \text{ H}_2\text{O} \,(g) + \text{ heat}
   \]

   a) Is this reaction **exothermic** or **endothermic**? (circle one)

   b) Is the entropy (randomness) of the system **increasing** or **decreasing**? (circle one)

   c) Label the sign (+ or −) of each variable in the equation below. If $\Delta G$ depends on the temperature, enter a question mark (?).

   \[
   \Delta G = \Delta H - T \Delta S
   \]

   $(-)$  $(−)$  $(−)$  $(+) (−)$

   d) At what temperatures is the reaction above spontaneous? (circle one)

      **at all temperatures**  **only spontaneous at high temperatures**  **only spontaneous at low temperatures**  **at no temperatures**

      (always spontaneous)  (never spontaneous)
3. Based on the following equation:

\[ \text{NH}_4\text{Cl} (s) + \text{heat} \rightarrow \text{NH}_4^+ (aq) + \text{Cl}^- (aq) \]

a) Is this reaction **exothermic** or **endothermic**? (circle one)

b) Is the entropy (randomness) of the system **increasing** or **decreasing**? (circle one)

3. **Heat** is absorbed as a reactant

\[ \Delta G = \Delta H - T \Delta S \]

\[ (??) = (+) - (+)(+) \]

c) Label the sign (+ or –) of each variable in the equation below. If \( \Delta G \) depends on the temperature, enter a question mark (??).

\[ \Delta G = \Delta H - T \Delta S \]

\[ (??) = (+) - (+)(+) \]

d) At what temperatures is the reaction above spontaneous? (circle one)

- **At all temperatures** (always spontaneous)
- **Only spontaneous at high temperatures**
- **Only spontaneous at low temperatures**
- **At no temperatures** (never spontaneous)

High temperatures allow the favorable \( \Delta S \) term to dominate in magnitude over the unfavorable \( \Delta H \) term.

4. The 150.0 g of water in a cup goes from 20.1°C to 48.5°C. How much heat was absorbed by the water?

\[ q = mC\Delta T \]

\[ q_w = m_w C_w (T_w \text{final} - T_w \text{initial}) \]

\[ q_w = (150.0 \text{ g}) (4.184 \text{ J/g}^\circ \text{C}) (48.5^\circ \text{C} - 20.1^\circ \text{C}) \]

\[ q_w = (150.0 \text{ g}) (4.184 \text{ J/g}^\circ \text{C}) (28.4^\circ \text{C}) \]

\[ q_w = 17823.84 \text{ J} \]

Answer: **17,800 J** or **1.78 \times 10^4 \text{ J}**

5. A 28.5 g piece of metal at 99.8°C is placed in a calorimeter containing 50.0 g of water at 22.3°C. The calorimeter itself has a heat capacity of 3.40 J/°C, and the temperature rises to 26.1°C. Calculate the specific heat of the metal (J/g°C).

\[ m_w C_w (T_{\text{final}} - T_{w \text{initial}}) + m_c C_c (T_{\text{final}} - T_{c \text{initial}}) = -m_x C_x (T_{\text{final}} - T_{x \text{initial}}) \]

\[ (50.0 \text{ g}) (4.184 \text{ J/g}^\circ \text{C}) (26.1^\circ \text{C} - 22.3^\circ \text{C}) + (3.40 \text{ J/}^\circ \text{C}) (26.1^\circ \text{C} - 22.3^\circ \text{C}) = - (28.5 \text{ g}) C_x (26.1^\circ \text{C} - 99.8^\circ \text{C}) \]

\[ (50.0 \text{ g}) (4.184 \text{ J/g}^\circ \text{C}) (3.8^\circ \text{C}) + (3.40 \text{ J/}^\circ \text{C}) (3.8^\circ \text{C}) = - (28.5 \text{ g}) C_x (-73.7^\circ \text{C}) \]

\[ (794.96 \text{ J}) + (12.92 \text{ J}) = - (-2100.45 \text{ g}^\circ \text{C}) C_x \]

\[ (807.88 \text{ J}) = (2100.45 \text{ g}^\circ \text{C}) C_x \]

Answer: **0.38 J/g°C**  \[ C_x = 0.3846223428 \text{ J/g}^\circ \text{C} \]**
6. 38.1 g of zinc and 25.9 g of aluminum are heated to 100.2°C, and dropped into a container with 200.0 g of water at 22.4°C. Assuming that no heat is lost, what is the final temperature of the water? Note: C_{Al} = 0.897 J/g°C and C_{Zn} = 0.388 J/g°C

\[
q_w = -(q_{Zn} + q_{Al})
\]

\[
m_w C_w (T_f - T_{w1}) = - (m_{Zn} C_{Zn} (T_f - T_{Zn1}) + m_{Al} C_{Al} (T_f - T_{Al1}))
\]

\[
(200.0 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(T_f - 22.4\text{ ºC}) = - ((38.1 \text{ g})(0.388 \text{ J/g} \cdot \text{°C})(T_f - 100.2\text{ ºC}) + (25.9 \text{ g})(0.897 \text{ J/g} \cdot \text{°C})(T_f - 100.2\text{ ºC}))
\]

\[
836.8 \text{ J/°C } T_f - 18744.32 \text{ J} = - (14.7828 \text{ J/°C } T_f - 1481.23656 \text{ J} + 23.2323 \text{ J/°C } T_f - 2327.87646 \text{ J})
\]

\[
874.8151 \text{ J/°C } T_f = 22553.43302 \text{ J}
\]

\[
T_f = 25.78079987\text{ ºC}
\]

Answer: \(25.8\text{ ºC}\)

7. Given the equation below, determine how many grams of methane (CH\(_4\)) must be combusted in a Bunsen burner to bring a beaker with 325.7 g of water at 24.3°C up to the normal boiling point? Assume that all of the heat generated by the burner is absorbed by the water.

\[
\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) + 891 \text{ kJ}
\]

\[
q_w = m_w C_w (T_{w f} - T_{w i})
\]

\[
q_w = (325.7 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(100.0\text{ ºC} - 24.3\text{ ºC}) = 103158.5702 \text{ J}
\]

\[
103158.5702 \text{ J} \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \left( \frac{1 \text{ mol CH}_4}{16.0426 \text{ g CH}_4} \right) \left( \frac{1 \text{ mol CH}_4}{1 \text{ mol CH}_4} \right) = 1.857386844 \text{ g CH}_4
\]

Answer: \(1.86 \text{ g CH}_4\)

8. A 79.3 L sample of a gas, at a constant pressure of 2.05 atm, absorbs 0.695 kJ of heat and expands to 82.1 L. What is the change in internal energy of the gas in joules?

\[
\Delta E = q + w = q - p \Delta V
\]

\[
\Delta E = 0.695 \text{ kJ} \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) + -(2.05 \text{ atm})(82.1 \text{ L} - 79.3 \text{ L}) \left( \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right)
\]

\[
\Delta E = 695 \text{ J} - 581.462 \text{ J} = 113.538 \text{ J}
\]

Answer: \(110 \text{ J or } 1.1 \times 10^2 \text{ J}\)
9. Given the following data, use Hess’s Law to calculate the $\Delta H$ for the overall reaction:

\[
\begin{align*}
\text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow \text{H}_2\text{O}_2(\text{aq}) & \Delta H = -191.2 \text{ kJ} \\
\text{C}_6\text{H}_4\text{O}_2(\text{aq}) + \text{H}_2(\text{g}) & \rightarrow \text{C}_6\text{H}_4(\text{OH})_2(\text{aq}) & \Delta H = -177.4 \text{ kJ} \\
\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) & \rightarrow \text{H}_2\text{O}(\text{g}) & \Delta H = -241.8 \text{ kJ} \\
\text{H}_2\text{O}(\text{g}) & \rightarrow \text{H}_2\text{O}(\text{l}) & \Delta H = -43.8 \text{ kJ}
\end{align*}
\]

Overall reaction:

\[
\text{C}_6\text{H}_4(\text{OH})_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{C}_6\text{H}_4\text{O}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})
\]

Required work:

- rewrite the equations above with the correct orientation, multipliers, and $\Delta H$ values
- show that after cancelling, the sum of your reactions gives the desired overall reaction

\[
\begin{align*}
\text{C}_6\text{H}_4(\text{OH})_2(\text{aq}) & \rightarrow \text{C}_6\text{H}_4\text{O}_2(\text{aq}) + \text{H}_2(\text{g}) & \Delta H = -1 \text{ }(-177.4 \text{ kJ}) \\
\text{H}_2\text{O}_2(\text{aq}) & \rightarrow \text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \Delta H = -1 \text{ }(-191.2 \text{ kJ}) \\
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2 \text{H}_2\text{O}(\text{g}) & \Delta H = 2 \text{ }(-241.8 \text{ kJ}) \\
2 \text{H}_2\text{O}(\text{g}) & \rightarrow 2 \text{H}_2\text{O}(\text{l}) & \Delta H = 2 \text{ }(-43.8 \text{ kJ})
\end{align*}
\]

\[
\text{C}_6\text{H}_4(\text{OH})_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{C}_6\text{H}_4\text{O}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})
\]

\[
\Delta H = -202.6 \text{ kJ}
\]

Answer: \(-202.6 \text{ kJ}\)

10. Using the provided $\Delta H_f^\circ$ values, calculate $\Delta H_{\text{rxn}}^\circ$ for the following reaction:

Note: $\Delta H_f^\circ \text{NH}_3(\text{g}) = -46 \text{ kJ/mol}$, $\Delta H_f^\circ \text{NO(g)} = 90 \text{ kJ/mol}$, and $\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) = -242 \text{ kJ/mol}$

\[4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}_2(\text{g})\]

\[
\Delta H_{\text{rxn}}^\circ = \Sigma [n \Delta H_f^\circ \text{(products)}] - \Sigma [n \Delta H_f^\circ \text{(reactants)}]
\]

\[
\Delta H_{\text{rxn}}^\circ = [n_{\text{NO}} \Delta H_f^\circ \text{NO}_2(\text{g}) + n_{\text{H}_2\text{O}} \Delta H_f^\circ \text{H}_2\text{O}_2(\text{g})] - [n_{\text{NH}_3} \Delta H_f^\circ \text{NH}_3(\text{g}) + n_{\text{O}_2(\text{g})} \Delta H_f^\circ \text{O}_2(\text{g})]
\]

\[
\Delta H_{\text{rxn}}^\circ = [4 \text{ mol } (90 \text{ kJ/mol}) + 6 \text{ mol } (-242 \text{ kJ/mol})] - [4 \text{ mol } (-46 \text{ kJ/mol}) + 5 \text{ mol } (0 \text{ kJ/mol})]
\]

\[
\Delta H_{\text{rxn}}^\circ = -1092 \text{ kJ} - (-184 \text{ kJ})
\]

\[
\Delta H_{\text{rxn}}^\circ = -908 \text{ kJ}
\]

Answer: \(-908 \text{ kJ}\)
11. Ethane, \( \text{C}_2\text{H}_6 \) (\( \text{H}_3\text{C}–\text{CH}_3 \)), is burned in air. Write the balanced equation, and calculate \( \Delta H^\circ_{\text{Rxn}} \) using the average bond energies provided.

\[
2 \text{C}_2\text{H}_6 + 7 \text{O}_2 \rightarrow 4 \text{CO}_2 + 6 \text{H}_2\text{O}
\]

Check:
- C 4 ✓
- H 12 ✓
- O 14 ✓
- Charge 0 ✓

\( \Delta H^\circ_{\text{Rxn}} = \Sigma [ \text{n (B.E. reactants)}] - \Sigma [ \text{n (B.E. products)}] \)

\[
\Delta H^\circ_{\text{Rxn}} = [2(\text{C–C}) + 12(\text{C–H}) + 7(\text{O=O})] - [8(\text{C=O}) + 12(\text{O–H})]
\]

\[
\begin{align*}
\Delta H^\circ_{\text{Rxn}} &= [2 \text{ mol}(347 \text{ kJ/mol}) + 12 \text{ mol}(413 \text{ kJ/mol}) + 7 \text{ mol}(498 \text{ kJ/mol})] - [8 \text{ mol}(799 \text{ kJ/mol}) + 12 \text{ mol}(467 \text{ kJ/mol})] \\
&= [9136 \text{ kJ}] - [11996 \text{ kJ}]
\end{align*}
\]

\[
\Delta H^\circ_{\text{Rxn}} = -2860. \text{kJ}
\]

Answer: \( -2860. \text{kJ} \)