1) Write equations for which the enthalpy change is the standard heat of formation per mole of the following compounds:

(a) HCl(g)

\[
\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})
\]

(3 points)

(b) N\textsubscript{2}O(g)

\[
\text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g})
\]

(3 points)

(c) CaCO\textsubscript{3}(s)

\[
\text{Ca}(s) + \text{C}(s) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CaCO}_3(s)
\]

(3 points)

(d) CH\textsubscript{3}OH(l)

\[
\text{C}(s) + 2\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(l)
\]

(3 points)
2) Without performing calculations, state whether the entropy of the system increases or decreases during each of the processes below. **For each explain your reasoning.**

a) oxidation of nitrogen: \( \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) \)  

- **Decrease** \( \boxed{2} \)
- A gas phase mole decreases from \( \boxed{2} \) reactant to products.

b) sublimation of dry ice: \( \text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g}) \)  

- **Increase** \( \boxed{1} \)
- Entropy of a gas typically greater than entropy of solid. Gas molecules are free to move around. Molecules in the solid phase \( \boxed{2} \).

c) the evaporation of water from damp clothes  

- **Increase** \( \boxed{2} \)
- Water molecules trapped in the clothes have less entropy than water molecules in the vapor phase. Free to move around. \( \boxed{2} \)
3) Although it is true that many spontaneous processes can be understood in terms of their moving in the direction that minimizes energy, not all spontaneous chemical reactions are exothermic. Explain how it is that an endothermic process can occur spontaneously. (9 points)

For a reaction to be spontaneous \( \Delta G < 0 \)

\[ \Delta G_v = \Delta H_v - T \Delta S_v \]

Sign of \( \Delta G_v \) depends on sign and relative magnitude of \( \Delta H_v \) and \( \Delta S_v \)

For an endothermic reaction \( \Delta H > 0 \)

if \( \Delta S_v > 0 \) and \( T \Delta S_v > \Delta H_v \)

then \( \Delta G_v < 0 \) \( \Rightarrow \) spontaneous
4) Water expands when it freezes. How much work (in kJ) does 100g of water do when it freezes at 0°C and bursts a water pipe with an opposing pressure of 1070 atm? The densities of H₂O(l) and H₂O(s) at 0°C are 1.00 and 0.92 g/cm³, respectively. (10 points)

\[ \text{work} = -p_{\text{ext}} \Delta V \quad (2) \]

\[ p_{\text{ext}} = 1070 \text{ atm} \quad (1) \]

\[ \Delta V = V_{\text{H₂O(s)}} - V_{\text{H₂O(l)}} \quad (1) \]

\[ V_{\text{H₂O(s)}} = \frac{100.0 \text{ g}}{0.92 \text{ g/cm}³} = 109 \text{ cm}³ = 0.109 \text{ L} \quad (2) \]

\[ V_{\text{H₂O(l)}} = \frac{100.0 \text{ g}}{1.00 \text{ g/cm}³} = 100 \text{ cm}³ = 0.100 \text{ L} \quad (2) \]

\[ \Delta V = 0.009 \text{ L} \]

\[ \text{work} = - (1070 \text{ atm}) (0.009 \text{ L}) \]

\[ = -9.63 \text{ L-atm} \]

\[ = -976 \text{ J} = -0.976 \text{ kJ} \]
5) Consider the synthesis of propane, C₃H₈, a gas used as camping fuel:

\[ 3 \text{C(s)} + 4 \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g}) \]

It is difficult to measure the enthalpy change of this reaction. However, standard enthalpies of combustion reactions are easy to measure. Given the following experimental data, determine the enthalpy of formation of propane gas from C(s) and H₂(g):

- C₃H₈(g) + 5 O₂(g) → 3 CO₂(g) + 4 H₂O(l) \( \Delta H^\circ = -2220 \text{ kJ} \)
- C(s) + O₂(g) → CO₂(g) \( \Delta H^\circ = -394 \text{ kJ} \)
- H₂(g) + 1/2 O₂(g) → H₂O(l) \( \Delta H^\circ = -286 \text{ kJ} \)

(12 points)
6) Amino acids are the building blocks of protein molecules. Amino acids undergo combustion in the body to urea, carbon dioxide gas, and liquid water. Consider the heat liberated per mole of the amino acid glycine, \( \text{NH}_2\text{CH}_2\text{COOH(s)} \), when it undergoes combustion to urea \( \text{NH}_2\text{CONH}_2(s) \), carbon dioxide gas and liquid water. Compare this value with the heat of combustion liberated per mole of glucose, \( \text{C}_6\text{H}_12\text{O}_6(s) \), to carbon dioxide gas and liquid water. **Which is a better fuel for the body, glucose or glycine? Explain your choice of answer.**

In addition to the thermodynamic data listed in the tables, use the information below as necessary.
\[
\Delta H^\circ_{f} \text{ glycine (NH}_2\text{CH}_2\text{COOH(s))} = -532.9 \text{ kJ/mol}
\]
\[
\Delta H^\circ_{f} \text{ urea (NH}_2\text{CONH}_2(s)) = -333.51 \text{ kJ/mol}
\]
\[
\Delta H^\circ_{f} \text{ glucose (C}_6\text{H}_12\text{O}_6(s)) = -1268 \text{ kJ/mol}
\]

\[
2 \text{NH}_2\text{CH}_2\text{COOH(s)} + 3 \text{O}_2(\text{g}) \rightarrow \text{NH}_2\text{CONH}_2(s) + 3 \text{H}_2\text{O(l)} + 3 \text{CO}_2(\text{g})
\]

\[
\Delta H^\circ_v = 2 \Delta H^\circ_{f} \text{ (NH}_2\text{CH}_2\text{COOH(s))} + 3 \Delta H^\circ_{f} \text{ (H}_2\text{O(l))} + 3 \Delta H^\circ_{f} \text{ (CO}_2(\text{g))}
\]

\[
= -1306.21 \text{ kJ} - 2 \Delta H^\circ_{f} \text{ (NH}_2\text{CH}_2\text{COOH(s))}
\]

\[
\Delta H^\circ_{c} / \text{ mole NH}_2\text{CH}_2\text{COOH(s)} = -1306.21 \text{ kJ} / 2\text{ mol} = -653.1 \text{ kJ/mol}
\]

\[
c_6\text{H}_12\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6\text{H}_2\text{O(l)}
\]

\[
\Delta H^\circ_v = \Delta H^\circ_c = 6 \Delta H^\circ_{f} \text{ (CO}_2(\text{g))} + 6 \Delta H^\circ_{f} \text{ (H}_2\text{O(l))} - \Delta H^\circ_{f} \text{ (C}_6\text{H}_12\text{O}_6(\text{s))}
\]

\[
= 6(-393.50 \text{ kJ/mol}) + 6(-286 \text{ kJ/mol}) - (-1268 \text{ kJ/mol})
\]

\[
= -2809 \text{ kJ}
\]

Heat of combustion / mole of glucose \( \Delta H^\circ_c = -2809 \text{ kJ} \)

On a molar basis, glucose liberates more heat than glycine, hence glucose is a better fuel.
7) A typical bathtub can hold about 100 gallons of water. (1 gallon = 3.785 L). Estimate the mass (in grams) of natural gas that would be needed to be burned to heat the 100 gallons of water from 70°F (21°C) to 100°F (38°C). Assume that natural gas is pure methane, CH₄. Assume the density of water at 21°C = 1.00 g/cm³, and that the specific heat of water at 21°C is 4.184 J °C⁻¹ g⁻¹. (12 points)

Amount of heat required to cause the temperature of 100-gallon bath from 21°C to 38°C

\[ m_{\text{H}_2\text{O}} \cdot C_{\text{H}_2\text{O}} \cdot \Delta t \]

\[ m_{\text{H}_2\text{O}} = 100 \text{ gallons} \times \frac{3.785 \text{ L}}{\text{gallon}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1.003 \text{ g/cm}^3}{\text{g}} = 3.78 \times 10^5 \text{ g} \]

\[ C_{\text{H}_2\text{O}} = 4.184 \text{ J °C}^{-1} \text{ g}^{-1} \]

\[ \Delta t = 17°C \]

\[ 3.78 \times 10^5 \text{ g} \times 4.184 \text{ J °C}^{-1} \text{ g}^{-1} \times 17°C = 2.69 \times 10^7 \text{ J} \text{ or } 2.69 \times 10^4 \text{ kJ} \]

Heat liberated per mole of CH₄ when reacted in the reaction:combustion of CH₄ (g)

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

\[ \Delta H^\circ = \Delta H^\circ_{\text{CO}_2 (g)} + 2 \Delta H^\circ_{\text{H}_2\text{O} (l)} - \Delta H^\circ_{\text{CH}_4 (g)} \]

\[ = (-393.505 \text{ kJ/mol}) + 2 (-286 \text{ kJ/mol}) - (-74.9 \text{ kJ/mol}) \]

\[ = -890.6 \text{ kJ} \]

1 mole of CH₄ liberates -890.6 kJ

To generate 2.69x10⁴ kJ heat requires 30.2 moles CH₄

Amount of CH₄ (in grams) required = 984 g
8) Consider the transformation of C(graphite) to C(diamond)

\[ \text{C(graphite)} \rightarrow \text{C(diamond)} \]

This reaction is significant, not only because diamond is a valued gemstone, but also because diamond is very hard and serves as a coating material to prolong the life of drilling tools and other objects used in demanding environments.

Based on thermodynamic data explain why for all temperatures the transformation of graphite to diamond can never occur spontaneously under standard conditions of 1 bar (1 atm).

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

If \( \Delta H^\circ > 0 \) and \( \Delta S^\circ < 0 \) then
\[ \Delta G^\circ > 0 \text{ for all } T \text{ and hence never spontaneous} \]

For \( \text{C(graphite)} \rightarrow \text{C(diamond)} \)

\[
\Delta H^\circ = \Delta H^\circ_f (\text{C(diamond)}) = +1.90 \text{ kJ/mol}
\]

\[
\Delta S^\circ = S^\circ (\text{C(diamond)}) - S^\circ (\text{C(graphite)})
\]

\[ = 2.5 \text{ J/mol-K} - 5.7 \text{ J/mol-K} = -3.2 \text{ J/mol-K} \]

For \( \text{C(graphite)} \rightarrow \text{C(diamond)} \)

\[ \Delta H^\circ > 0 \text{ and } \Delta S^\circ < 0 \implies \Delta G^\circ > 0 \text{ for all } T \]

Hence \( \text{C(graphite)} \rightarrow \text{C(diamond)} \) is not spontaneous for all temperature.
9) a) From the plot of free energy versus temperature given below, explain why the liquid is never the stable phase, over the range of temperatures shown. (6 points)

For a phase transition to be spontaneous, \( DG < 0 \)

For a compound whose \( G \) of solid, liquid, gas phase varies with \( T \) as shown in the graph:

For all \( T \)  \( G_{\text{liquid}} > G_{\text{solid}} \) \( \Rightarrow \)  \( G_{\text{gas}} \)  \( \Rightarrow \)

Hence a phase transition of liquid \( \rightarrow \) solid has \( \Delta G > 0 \)

and a phase transition of liquid \( \rightarrow \) gas has a \( \Delta G > 0 \)

Hence the liquid is never the stable phase over the range of \( T \) shown.

9 b) For a compound whose free energy varies with temperature as shown in the above plot, what phase transition does the solid undergo as heat is supplied at constant pressure? Explain your choice of answer. (4 points)

Solid undergoes sublimation. The temperature at which \( G_{\text{solid}} = G_{\text{gas}} \) corresponds to \( T_{\text{sublimation}} \).

If \( T > T_{\text{sublimation}} \) then \( G_{\text{gas}} < G_{\text{solid}} \) and solid sublimes to gas.