1) Determine $\Delta H_f^\circ$ of ethanol (C$_2$H$_5$OH) from its standard enthalpy of combustion (-1367.4 kJ/mol to produce CO$_2$(g) and H$_2$O(l)). $[\Delta H_f^\circ (CO_2(g)) = -393.51 \text{kJ/mol}, \ \Delta H_f^\circ (H_2O(l)) = -285.83 \text{kJ/mol}]

The combustion reaction is:

$$\text{C}_2\text{H}_5\text{OH} + \frac{7}{2} \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad \Delta H = -1367.4 \text{kJ}$$

In terms of $\Delta H_f^\circ$, the reaction can be written:

$$\Delta H = 2\Delta H_f^\circ (\text{CO}_2) + 3\Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ (\text{C}_2\text{H}_5\text{OH}) - \frac{7}{2} \Delta H_f^\circ (\text{O}_2)$$

$-1367.4 = 2(-393.51) + 3(-285.83) - \Delta H_f^\circ (\text{C}_2\text{H}_5\text{OH}) - 0$

$$\Delta H_f^\circ (\text{C}_2\text{H}_5\text{OH}) = +1367.4 + 2(-393.51) + 3(-285.83)$$

$$= -277.1 \text{ kJ/mol}$$

2) Before the invention of polymer fillings, dentists used amalgams of mercury and silver to fill cavities. You would like the amalgam to have a temperature of 37°C, so it doesn’t hurt the patient when you put it in the cavity. You start with 1.20g of silver at 100.0°C. The mercury is initially at 25°C. How many grams of mercury must you mix with the silver to get a final temperature for the amalgam of 37°C? (The heat capacity of silver is 0.139 J/(g K), and that of mercury is 0.235 J/(g K).)

$$1.24 \text{ Ag} \quad 74^\circ \text{C} \quad 25^\circ \text{C} \rightarrow 1.24 \text{ Ag} \quad 37^\circ \text{C} \quad 37^\circ \text{C}$$

$$Q_{\text{Ag}} = -Q_{\text{Hg}}$$

$$1.24 \left(0.139 \frac{\text{J}}{\text{g} \cdot \text{K}}\right) \left(37^\circ - 100^\circ\right) = -m_{\text{Hg}} \left(0.235 \frac{\text{J}}{\text{g} \cdot \text{K}}\right) \left(37^\circ - 25^\circ\right)$$

$$m_{\text{Hg}} = \frac{(1.24) \left(0.139 \frac{\text{J}}{\text{g} \cdot \text{K}}\right) \left(37^\circ - 100^\circ\right)}{-\left(0.235 \frac{\text{J}}{\text{g} \cdot \text{K}}\right) \left(37^\circ - 25^\circ\right)} = 3.74$$
3) When a 4.50g sample of NH₄NO₃ is dissolved in 80.0g of water, the temperature drops from 22.0°C to 17.7°C. Calculate ΔH (in kJ/mole) for the solution process,

\[ \text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+ (\text{aq}) + \text{NO}_3^- (\text{aq}) \]

Assume that the solution does not exchange heat with its surroundings, and that the heat capacity of the solution is the same as that of pure water [1.00 cal/ (g °C) ]. Mol Wt (NH₄NO₃) = 80.0 g/mol

\[ Q_{\text{REACTION}} = -Q_{\text{H}_2\text{O}} \]

\[ Q_{\text{H}_2\text{O}} = (80 \text{ g} \text{ H}_2\text{O}) \left( 4.184 \frac{\text{J}}{\text{g} \cdot \text{K}} \right) (17.7 - 22.0) = -1440 \text{ J} \]

This heat is absorbed from the solution

\[ 4.50 \text{ g} \text{ NH}_4\text{NO}_3 \times \frac{1 \text{ mol}}{80.0 \text{ g}} = 0.0562 \text{ mole} \text{ NH}_4\text{NO}_3 \]

So the enthalpy of the reaction is

\[ \Delta H = \frac{-1440 \text{ J}}{0.0562 \text{ mole}} = -25.6 \text{ kJ/mole} \]

4) The specific heat of vaporization of a liquid (ΔHᵥₚ) is the energy required to vaporize 1.00g of the liquid at its boiling point. In one experiment, 60.0g of liquid nitrogen, at its boiling point of -196°C, are poured into a Styrofoam cup containing 2.00x10⁻² g of water at 55.3°C. Calculate the molar heat of vaporization of liquid nitrogen if the final temperature of the water is 41.0°C.
The heat from the water was:

\[ Q_{\text{H}_2\text{O}} = 200\, \text{g} \cdot (4.184\, \text{J/g} \cdot \text{K}) \cdot (41.0 - 55.3) = -11966\, \text{J} \]

This heat is sufficient to boil 60.0 g N\(_2\)

\[ 60.0\, \text{g N}_2 \left( \frac{\text{mole}}{28.0\, \text{g}} \right) = 2.14\, \text{mole} \]

So

\[ \Delta H_{\text{vap}} = \frac{12\, \text{kJ}}{2.14\, \text{mole}} = 5.6\, \text{kJ/mole} \]

5) Using the table of enthalpies of atomization and bond enthalpies in Lecture Notes C, please estimate \( \Delta H \) for the following reaction:

\[ \text{C}_2\text{H}_4(\ell) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH} (\ell) \]

Bond strengths from table (kJ/mole):

- C-H 413
- C-C 348
- C-O 351
- O-H 463
- C=C 615

\[ \Delta H = -34\, \text{kJ/mole} \]

Net since the reaction is down hill in \( \Delta H \).
6) Consider vaporizing 60.0 g of liquid nitrogen at its boiling point of -196°C. What is the entropy for this process (in J/K)?

$$\Delta H_{\text{vap}} (N_2) = 5.6 \text{ kJ/mole}$$

The heat required to boil 60.0 g $N_2$ is then

$$q = \left( \frac{5.6 \text{ kJ}}{\text{mole}} \right) \left( 60.0 \text{ g} \right) \left( \frac{1 \text{ mole}}{28.05 \text{ g}} \right) = 12.0 \text{ kJ}$$

Boiling a substance at the boiling point is the reversible path so $q_{\text{rev}} = 12.0 \text{ J}$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{12.0 \text{ kJ}}{77 \text{ K}} = 0.16 \text{ kJ/K}$$

7) Consider the following reaction:

$$H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O \ (g)$$

a) Use Table 7.3 (average bond enthalpies) to estimate $\Delta H$ for this reaction.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Strength (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>436</td>
</tr>
<tr>
<td>O=O</td>
<td>498</td>
</tr>
<tr>
<td>O-H</td>
<td>463</td>
</tr>
</tbody>
</table>

To calculate $\Delta H$:

$$\Delta H = \frac{2 \times 463 - 2 \times 498}{2} = -241 \text{ kJ/mol}$$

b) Use Appendix D to calculate $\Delta H$ and $\Delta S$ for this reaction.

$$\Delta H = -241.82 \text{ kJ/mol}; \quad \Delta S = -44.38 \text{ J/mol}$$
c) Is this reaction spontaneous at 25°C?

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

\[
= -241.82 \text{ kJ mol}^{-1} - (298 K) \left( -0.044 \text{ kJ mol}^{-1} \right)
\]

\[
= -241.82 \text{ kJ mol}^{-1} + 131 \text{ kJ mol}^{-1}
\]

**PROMINATES**

\[
\text{So } \Delta G < 0 \text{ SPONTANEOUS}
\]

d) Is this reaction enthalpy driven, entropy driven, driven by both enthalpy and entropy, or driven by neither?

\[
\text{ON CO ENTHALPY DRIVEN}
\]

\[
\text{OS CO NOT ENTROPY DRIVEN}
\]

g) A 1.00 liter vessel contains 0.0100 atm of H₂ (g) and 0.00500 atm of O₂ (g) and 10.0 atm of Argon. The container is sealed such that its volume is fixed at 1.00 liter and insulated such that that the gas does not exchange heat with the walls of the vessel or with the surroundings. The initial temperature is 25.0°C. The reaction shown above then occurs and goes to completion. What is the final temperature? (You can assume the heat capacity of the gas is that appropriate for a monatomic ideal gas.)

\[
\begin{align*}
\text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) & \rightarrow \text{H}_2 \text{O} (g) \\
\Delta H &= -241.82 \text{ kJ mol}^{-1}
\end{align*}
\]

**INITIAL**

\[
4.1 \times 10^{-4} \text{ mole} \quad 2.0 \times 10^{-4} \text{ mole}
\]

**FINAL**

\[
0 \
0 \
4.1 \times 10^{-4} \text{ mole}
\]

Heat given off by the reaction is

\[
241.82 \text{ kJ mol}^{-1} \left( 4.1 \times 10^{-4} \text{ mole} \right) = 0.10 \text{ kJ}
\]

This heat goes into the 10 atm gas. In constant V, the heat capacity of the gas is

\[
C_V = \frac{3}{2} R
\]
\[ m_{\Delta T} = \frac{(1.0 \text{ mJ})(1.008)}{(0.0821 \text{ mJ/kg K})(298 \text{ K})} = 0.41 \text{ mJ} \]

\[ Q_{\text{cal}} = 0.10 \text{ kJ} = mC_v \Delta T \]

\[ 100 \text{ J} = 0.41 \text{ mJ} \left( \frac{3}{2} \times 8.31 \frac{\text{J}}{\text{mol K}} \right) \Delta T \]

\[ \Delta T = \frac{100 \text{ J}}{(0.41 \text{ mJ}) \left( \frac{3}{2} \times 8.31 \frac{\text{J}}{\text{mol K}} \right)} = 20^\circ \text{C} \]

\[ \Delta T = 25^\circ \text{C} + 20^\circ \text{C} = 45^\circ \text{C} \]
Solutions to Review Problems 8-16 for Exam 1

8) A traveler goes from Pittsburgh, PA to Aspen, CO. Which of the following is a state function of the trip:
   a) distance travelled   b) elapsed time   c) altitude change
d) work done to move the vehicle   e) none of the items listed
   (c) is the only property that is independent of the path followed, so it is the only state function.

9) In the eighteenth century, soap was produced by reacting a base with either vegetable oil or animal fat. In producing the base, the first step was to obtain quicklime (CaO) by heating Calcium carbonate to 850°C. The reaction is:
   \[ \text{CaCO}_3(s) \rightarrow \text{CaO} (s) + \text{CO}_2(g) \]
   What is the sign of \( \Delta S \) for this reaction?
   The reaction is of the form: solid \( \rightarrow \) solid + gas. The evolution of the gas leads to a large increase in entropy (large positive \( \Delta S \))

   A base was obtained by mixing this with liquid water to give:
   \[ \text{CaO} (s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \]
   What is the sign of \( \Delta S \) for this reaction?
   The reaction of the form: solid + liquid \( \rightarrow \) solid. The conversion of the liquid to a solid leads to a small decrease in entropy (small negative \( \Delta S \))

10) Many homes in Pittsburgh are heated by burning natural gas (methane = CH\(_4\)) , to give CO\(_2\)(g) and H\(_2\)O(l). Without using Appendix D, what are the signs of \( \Delta H \) and \( \Delta S \) for this combustion reaction?
   The reaction is \( \text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O} (l) \). Since the reaction is used to heat homes, it must give off heat, so \( \Delta H < 0 \). The reaction is of the form 3 gas \( \rightarrow \) 1 gas + liquid. The loss of gas corresponds to a decrease in entropy (\( \Delta S < 0 \))

   Suppose that instead of producing H\(_2\)O(l), the reaction produced H\(_2\)O(g). What would happen to the magnitude of \( \Delta H \) for the combustion reaction? What would happen to \( \Delta S \) [is \( \Delta S < 0 \), \( \Delta S > 0 \), or \( \Delta S \) is not obvious (need Appendix D)]?
   The reaction is now \( \text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O} (g) \)
   -The liquefaction of water (H\(_2\)O(g) \( \rightarrow \) H\(_2\)O(l)) gives off heat, so this reaction (producing water vapor) gives off less heat than producing liquid water. So \( \Delta H \) for the reaction that produces water vapor is less negative (smaller magnitude) than the reaction that produces liquid water.
   -The reaction is now of the form 3 gas \( \rightarrow \) 3 gas, so \( \Delta S \) is small (we would need to use appendix D to determine its magnitude, and this shows it to be <0).

11) For which of the the following two reactions:
   A) \( \text{H}_2 (g) + 1/2 \text{O}_2 (g) \rightarrow \text{H}_2\text{O} (l) \)
   B) \( \text{H}_2 (g) + 1/2 \text{O}_2 (g) \rightarrow \text{H}_2\text{O} (g) \)
   Do you expect there to be a bigger difference between \( \Delta E \) and \( \Delta H \)?
   The change in number of moles of gas is bigger for A (1 ½ gas \( \rightarrow \) liquid) than for B (1 ½ gas \( \rightarrow \) 1 gas). So the pressure will change more for A than for B, and the PV part of H=E+PV will be larger in magnitude for A than B. So \( \Delta H \) and \( \Delta E \) will be more different for A.
12) The heat involved in a constant pressure process is equal to:
   a) $\Delta H$       b) $\Delta T$       c) $\Delta E$       d) $\Delta S$       e) $C_p$
   (a) This is the motivation for defining a quantity $H=E+PV$ (The change in $H$ is the heat associated with a constant pressure process).

13) If a process is both endothermic and spontaneous then:
   a) $\Delta S > 0$       b) $\Delta S < 0$       c) $\Delta H < 0$       d) $\Delta G > 0$       e) $\Delta E = 0$
   If the reaction is endothermic, it is not enthalpy driven. So if it is spontaneous, then it must be entropy-driven, and so $\Delta S > 0$.

14) Which of the following has the greatest third law molar entropy:
   a) C(diamond)       b) Pb (solid)       c) Hg (liquid)       d) Hg (gas)
   We didn’t get to this in class, so this question is cancelled (the answer is (d), since gases have large third law entropy’s).

15) Sulfur dioxide ($SO_2$) is used as a preservative, a bleaching agent, and in the paper industry. Consider the following reactions and their corresponding $\Delta G$’s,
   $$SO_2(g) + \frac{1}{2} O_2(g) \rightarrow SO_3(g) \quad \Delta G_1$$
   $$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g) \quad \Delta G_2$$
   What is the relationship between $\Delta G_1$ and $\Delta G_2$.
   Reaction 2 is twice the reverse of reaction 1, so we need to change the sign of $\Delta G$ and multiply it by two. $\Delta G_2 = -2 \Delta G_1$.

16) For which of the following substances does $\Delta H^\circ_f=0$ (circle all that apply) ?
   a) Br$_2$(g)       b) N(g)       c) C(g)       d) CO(g)       e) Ne(g)
   The heat of formation will be zero for an element that is in its standard state. This is true only for (e).
   a) Br$_2$ is a liquid at room temperature, so the gas is not the standard state.
   b) N is N$_2$ at room temperature
   c) C is graphite in its most stable form at room temperature
   d) CO is not an element
   e) Ne is a gas at room temperature, so (e) is an element in its standard state.