1. (20 points) Consider the combustion of propane \([C_3H_8\ (g)]\) to form \(H_2O(g)\) and \(CO_2(g)\).

\[
C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)
\]  

(a) Using the thermodynamic data provided in Table 4.3 (attached), to calculate \(\Delta_r H\) and \(\Delta_r U\) for the combustion of 1 mole of propane at 298 K and 1 Bar (which is approximately 1 atm).

\[
\Delta_r H = 3 \Delta_f H(CO_2) + 4 \Delta_f H(H_2O) - \Delta_f H(C_3H_8) - 5 \Delta_f H(O_2) \\
= 3(-393.5) + 4(-241.8) - (-103.8) + 5(0) \\
= -2043.9 \text{ kJ}
\]

\[
\Delta_r U = \Delta_f H - \Delta n_g RT \\
= -2043.9 - 1 \times 8.314 \times 298 \times 10^{-3} \\
= -2946.4 \text{ kJ}
\]

(b) Approximate the molar heat capacities at constant pressure \(C_P\) of all four species involved in this reaction at 298 K.

For a linear molecule, \(C_v \approx \frac{5}{2}R\) and \(C_P \approx \frac{7}{2}R\).

For a nonlinear molecule, \(C_v \approx 3R\) and \(C_P \approx 4R\).

Both of the above equations neglect vibrations because only the lowest vibrational state is expected to be populated in these molecules at 298 K.

(c) If the temperature of the system is increased at constant pressure will \(\Delta_r H\) increase, decrease or remain constant? Justify your answer. (you may assume that the heat capacities are constant over the temperatures sampled in the experiment.)

\[
\Delta C_P = 3 \times \frac{7}{2}R + 4 \times 4R - 4R - 5 \times \frac{7}{2}R > 0
\]

Therefore \(\Delta_r H(T_2) - \Delta_r H(T_1) = \Delta C_P \Delta T\) is positive for positive \(\Delta T\), or \(\Delta_r H\) increases with increasing \(T\).
2. (10 points) A lab worker had three gas cylinders. One she knew contained neon, but the other two had no identifying labels. She allowed all three gases to effuse through an orifice and recorded the following observations:

<table>
<thead>
<tr>
<th>gas</th>
<th>effusion time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>5.00 min</td>
</tr>
<tr>
<td>A</td>
<td>5.90 min</td>
</tr>
<tr>
<td>B</td>
<td>2.25 min</td>
</tr>
</tbody>
</table>

(a) What are the molecular weights of gases A and B?

\[
\frac{r_2}{r_1} = \frac{t_1}{t_2} = \sqrt{\frac{m_1}{m_2}}
\]

As a result,

\[
m_1 = \left(\frac{t_1}{t_2}\right)^2
\]

For A:

\[
m_1 = 20.179 \times \left(\frac{5.90}{5.00}\right)^2 = 28.10
\]

For B:

\[
m_1 = 20.179 \times \left(\frac{2.25}{5.00}\right)^2 = 4.086
\]

(b) Propose reasonable chemical identities for gases A and B based on their molecular weights.

Possible identities for A are N\(_2\) or CO.

B could reasonably be either D\(_2\) or He.
3. (15 points) For each of the following thermodynamic processes indicate the sign of the specified thermodynamic quantities. Briefly justify your answers.

(a) For an adiabatic, reversible expansion of an ideal gas, indicate if $\Delta U_{\text{rev}}, \Delta H_{\text{rev}}, q_{\text{rev}}$ and $w_{\text{rev}}$ are positive, negative or zero.
   For an adiabatic process $q = 0$
   For an expansion $w < 0$
   Since $\Delta U = q + w = w$, $\Delta U < 0$
   Since $\Delta U < 0$ and $\Delta U \propto \Delta T$, $\Delta T < 0$.
   With a decrease in temperature $\Delta H < 0$

(b) For an adiabatic, irreversible expansion of an ideal gas with the same initial and final conditions as in part (a), indicate if $\Delta U_{\text{irrev}}, \Delta H_{\text{irrev}}, q_{\text{irrev}}$ and $w_{\text{irrev}}$ are larger than, smaller than or equal to the corresponding values for the reversible process.
   This question is ill-posed. It is impossible for the initial and final conditions to be the same and for the process to be adiabatic! Everyone was given full credit for this part.

(c) For the chemical reaction demonstrated the first day of class:

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g})$$

(2)

indicate the signs of $\Delta U, \Delta H, q$ and $w$.
This is an endothermic reaction and $\Delta H < 0$
Since the reaction takes place at constant $P$, $q = q_p = \Delta H < 0$
Since for this reaction $\Delta n_g < 0$, $w > 0$.
$\Delta U = q + w$ but $|q| >> w$ making $\Delta U > 0$.
4. (20 points) For each of the following statements, signify agreement or disagreement. For either answer, provide support in the form of a statement, an explanation, an equation or a derivation. In the case of disagreement, you may also provide a contradictory example.

(a) For an ideal gas, \( C_V = \frac{3}{2} R \).
   Only for a monoatomic gas. **DISAGREE**

(b) For most efficient use, the freezer should be kept fully packed with food.
   **AGREE.** The heat capacity of the contents of the freezer is much larger for food than for air (if for no other reason than because the number of moles of food is much larger than the number of moles of air). Therefore, it is much harder to change the temperature of the freezer when it is full than when it is empty, making it much easier to maintain a constant temperature.

(c) \( \Delta H = q_P \)
   This is a definition. \( \Delta H \) is the heat that would be absorbed by a process at constant pressure! **AGREE**

(d) According to kinetic molecular theory, the time required for a molecule to travel between two points that are a distance \( l \) apart is \( l/c_{\text{rms}} \). **DISAGREE**
   In fact, to move a macroscopic distance, the molecules will undergo collisions making the time much larger than \( l/c_{\text{rms}} \)
5. (15 points) Answer the following questions based on information provided in Figs. 1 and 2 in the attached information sheets.

(a) Provide the signs of $B'$ and $C'$ for $\text{H}_2$ based on the curve in Fig. 1, where

$$Z = 1 + B'P + C'P^2$$

Both $B'$ and $C'$ are positive.

(b) In Fig. 1, explain why $Z > 1$ for $\text{H}_2$ even at very low pressures?

Repulsive interactions among molecules are more important than attractive ones (increasing $P\overline{V}$ relative to $nRT$). Another way to say this is that the correction due to the finite size of the $\text{H}_2$ molecules is more important than the attractive interactions. For larger systems with larger volumes and dipole moments, the intermolecular attractions dominate at low $P$.

(c) In Fig. 2, three Boltzman distributions have been plotted for the conditions:

<table>
<thead>
<tr>
<th>molecule</th>
<th>$T$ (in K)</th>
<th>curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{He}$</td>
<td>500</td>
<td>C</td>
</tr>
<tr>
<td>$\text{Ne}$</td>
<td>500</td>
<td>A</td>
</tr>
<tr>
<td>$\text{He}$</td>
<td>250</td>
<td>B</td>
</tr>
</tbody>
</table>

Indicate which curve corresponds to each of the sets of conditions and justify your choices with words or equations.

The curves shift to the right with increased mass or decreasing $T$ because

$$c_{mp} \propto \sqrt{\frac{T}{M}}$$

Therefore, curve C must be $\text{He}$ at 500 K.

Increasing the mass by a factor of 5 will have a larger effect on $c_{mp}$ than dividing the temperature in half. Therefore, B is $\text{He}$ at 250 K and A is $\text{Ne}$ at 500 K.
6. (20 points) Consider a 1.00 L gas sample, initially at 10 atm, 298 K is allowed to expand. For each of the conditions described below, calculate $\Delta U$, $q$ and the final volume of the sample ($C_v = 3/2R$).

(a) The gas is allowed to expand isothermally against a constant external pressure of 1 atm.

$$n = \frac{PV}{RT} = \frac{10 \times 1}{0.08206 \times 298} = 0.4089 \text{ mol}$$

At constant $T$ $P_i V_i = P_f V_f$ making $V_f = 10$ L.

$$q = -w = P_{ex}(V_f - V_i) = 9 \text{ L atm} = 912 \text{ J}$$

For an isothermal process $\Delta U = 0$.

(b) The gas is allowed to expand isothermally and reversibly so that the final pressure is 1 atm.

Since the initial and final conditions are the same as in part (a), $\Delta U = 0$ and $V_f = 10$ L.

$$q = nRT \ln \left( \frac{V_f}{V_i} \right) = 0.4089 \times 8.314 \times 298 \ln(10) = 2330 \text{ J}$$

(c) The gas is allowed to expand adiabatically and reversibly to a final pressure of 1 atm.

For an adiabatic process,

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

$$V_f = \left( \frac{P_i}{P_f} \right)^{3/5} V_i = 3.98 \text{ L}$$

$$T_f = \frac{PV}{nR} = \frac{1 \times 3.98}{0.4089 \times 298} = 119 \text{ K}$$

$$\Delta U = nC_v \Delta T$$

$$= 0.4089 \times \frac{3}{2} \times 8.314 \times (119 - 298) = -915 \text{ J}$$