Part 1: (18 points) Define or explain three out of the 6 terms

a) Carnot cycle. Define and give an important result of this cycle.

**Answer:** A hypothetical heat engine, consisting of a four step thermodynamic cycle. The cycle is composed of a reversible isothermal expansion, followed by a reversible adiabatic expansion, then a reversible isothermal contraction and a reversible adiabatic contraction back to the initial state. An important result is the limiting efficiency for which heat engines can convert heat to work… \( \varepsilon = \frac{T_H - T_L}{T_H} \) where \( T_H \) is the temperature of the high T reservoir and \( T_L \) is the temperature of the low T reservoir.

b) Isothermal compressibility. Define in terms of state variables \( P, V, \) and/or \( T \) and give a physical description.

**Answer:** The fractional change in volume of a substance when pressure is applied at constant temperature. \( \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \).

c) Perpetual motion machines. Define and state how and why these devices violate the thermodynamic laws.

**Answer:** A perpetual motion machine of the first kind is exemplified by a generator which powers an electric motor, which in turn powers the generator and at the same time produces work. Thus a closed cycle device makes work. It violates the first law’s proscription against creating or destroying energy. A perpetual motion machine of the second kind has the net effect of transferring heat from a cold reservoir to a hot reservoir. It does not violate the first law because energy is conserved, but the entropy of the universe decreases and thus the operation of this engine violates the second law.

d) Maxwell Relations. Give mathematical expressions and explain how these equations are used in thermodynamics.

\[
\left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V \quad \text{... from } dE = TdS - PdV \\
\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad \text{... from } dH = TdS + VdP \\
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{... from } dA = -SdT - PdV \\
\left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \quad \text{... from } dG = -SdT + VdP
\]

These equations are used to convert all thermodynamic derivatives into functions of \( P, T, V, \alpha, \kappa, \) or \( \tilde{c}_p \).
e) Define entropy as the term is used in the field of thermodynamics.
Answer: Anything reasonable and well thought out. If you use “entropy is time’s arrow” you had better make a clear explanation of what you mean.

f) Exact and inexact differentials. Define the terms as they are used in mathematics. Explain how exact and inexact differentials are used in thermodynamics. How are their properties physically relevant?
Solution: A differential has the form \[ M(x, y)\, dx + N(x, y)\, dy \]. If the differential is exact it can be expressed as
\[
\frac{\partial Z}{\partial x} \bigg|_y \, dx + \frac{\partial Z}{\partial y} \bigg|_x \, dy
\]
and so an exact differential fulfills Euler’s criterion i.e.
\[
\frac{\partial M}{\partial y} \bigg|_x = \frac{\partial N}{\partial x} \bigg|_y.
\]
The line integrals of exact differentials are independent of path, and this property is important for state functions, which can be represented as exact differentials. Therefore \( E, H, S, G, \) and \( A \) are exact differentials. Inexact differentials are path dependent when integrated and in thermodynamics include work \( w \) and heat \( q \).

Part 2 (20 points) Answer two out of the four questions below. Answers should be no longer than 200 words.

a) Two cannons with identical iron barrels are filled with identical amounts of gun powder. One cannon is loaded with a heavy iron cannon ball…while the other cannon is not loaded. Both cannons are fired. The loaded cannon expels its cannon ball. After firing, will the temperatures of the two cannon barrels be the same? If they are not the same which is hotter? Explain your answer using the Laws of Thermodynamics.
Solution: From the First Law \( \Delta E=q+w \). The energy released as a result of the firing (explosion of the gun powder) is manifested as heat and work done in moving the cannon ball. Much less work is performed in the unloaded cannon so the unloaded cannon heats up more. (47 words)

b) Before the days of electricity, clothes were pressed with flatirons, that were literally made of iron and heated on a stove. A flatiron was very heavy, despite the fact that anyone could show that it was the heat and not the weight of the flatiron that took wrinkles out of clothes. Explain why flatirons had to be heavy.
Solution: The heat transferred to the clothes from the flatiron is \( q=MxCx\Delta T \), where \( M \) is the mass of the flatiron, \( C \) is the specific heat of the flatiron, and \( \Delta T \) is the temperature change in the flatiron resulting from the transfer of heat to the cloth. The heat transfer can be maximized either by raising the temperature of the flatiron or by increasing its mass. The former approach must be limited by the necessity of not burning the cloth, so increasing the mass of the flatiron is the only practical method. (90 words)
c) Suppose the equilibrium length of a spring is $x_0$. If the spring is coiled up such that its length is changed by $x$ from its equilibrium position its potential energy is 
\[
\frac{1}{2} \kappa (x - x_0)^2
\]
where $\kappa$ is the spring constant. Two identical springs (i.e. identical $x_0$, $\kappa$, and masses) are dissolved completely in acid. If one spring is coiled up before dissolving in acid and the other is not coiled up, will the heats of reaction be the same or different. If the heats of reactions are different, which reaction gives off more heat, the dissolving of the coiled up spring or the uncoiled spring? Explain you answer using the Laws of Thermodynamics.

Solution: All other things being equal, the heat of reaction of the coiled-up spring must be higher. If the spring is coiled up the potential energy must be higher than that of the spring at its uncoiled, equilibrium length. The potential energy cannot be destroyed by dissolving the spring, so it must be converted into some other form, which is heat. (60 words)

d) Rubber is an elastic substance composed of chain-like organic polymers. In an unstretched rubber band, the polymers are coiled up like a pile of cooked noodles, but when the rubber band is stretched the polymer chains are lined up in a more or less parallel fashion (like uncooked spaghetti). Suppose a small weight is suspended from a bar by a rubber band. After the rubber band and weight come to thermal and mechanical equilibrium with the surroundings, warm air is blown over the rubber band. Assuming the rubber band is not burned nor undergoes any chemical reaction of any kind as a result of the heating, will the rubber band contract in length, stretch, or remain the same when it is heated? Explain your answer in terms of the Laws of Thermodynamics and the state functions whose changes are governed by those laws. If appropriate describe how state functions change (qualitatively) in the system (i.e. the rubber band) and the surroundings.

Solution: Heat is transferred $\Delta S_{surr} = \frac{q_{rev}}{T_{surr}} < 0$. Therefore $\Delta S_{sys} > 0$. The high entropy state of the polymer is the coiled-up state, so upon warming the rubber band will actually contract. (26 words).

Part 3: (30 points) Perform two out of the four calculations given below.

a) For oxygen gas $O_2$ between the temperatures of $T=298K$ and $T=2000K$, the heat capacity has the empirically-derived form
\[
C_p = 29.93 + 4.18 \times 10^{-3}T - 1.67 \times 10^5 T^{-2}
\]
The units are Joules/K-mole. Calculate the entropy change that results from increasing the temperature of one mole of oxygen gas from 298K to 1000K.

Hint: $\int x^n \, dx = \frac{x^{n+1}}{n+1} \ldots n \neq -1$.

Solution:
\[ S_{1000} - S_{298} = \int_{298}^{1000} \frac{C_p}{T} dT = \int_{298}^{1000} \frac{1}{T} \left( 29.93 + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \right) dT \]

\[ = \int_{298}^{1000} \left( \frac{29.93}{T} + 4.18 \times 10^{-3} - 1.67 \times 10^5 T^{-3} \right) dT \]

\[ = 29.93 \ln\left( \frac{1000}{298} \right) + \left( 4.18 \times 10^{-3} \right) (1000 - 298) + 0.84 \times 10^5 \left( 1000^{-2} - 298^{-2} \right) \]

\[ = 38.37 \text{J/K} \]

b) Iron pellets with a total mass of 17 grams at a temperature of 370K are mixed in an insulated container with 17 grams of water at a temperature of 293K. The heat capacity per gram of water is ten times that of the iron. What is the temperature of the iron and the water when they reach thermal equilibrium?

Solution: The iron is at a higher temperature so heat flows from the iron to the water. Therefore

\[ q_{\text{iron}} = q_{\text{water}} \Rightarrow -m_{\text{iron}} C_p \text{iron} \left( T_f - 370K \right) = m_{\text{water}} C_p \text{water} \left( T_f - 293K \right) \]

\[ -m_{\text{iron}} C_p \text{iron} \left( T_f - 370K \right) = m_{\text{water}} 10 C_p \text{iron} \left( T_f - 293K \right) \]

\[ -\left( T_f - 370K \right) = 10 \left( T_f - 293K \right) \ldots \text{note} \ m_{\text{iron}} = m_{\text{water}} \]

\[ T_f = \frac{370K + 2930K}{11} = 300K \]

\[ \]

c) Calculate the work done when one mole of an ideal monatomic gas at an initial temperature of T=298K and an initial pressure of 10 atm expand adiabatically and reversibly until the final pressure is 1 atm.

Solution:

\[ P_1 V_1^r = P_2 V_2^r \Rightarrow P_1 \left( \frac{T_1}{P_1} \right)^r = P_2 \left( \frac{T_2}{P_2} \right)^r \]

\[ P_1^{1-r} T_1^r = P_2^{1-r} T_2^r \Rightarrow T_2 = T_1 \left( \frac{P_1}{P_2} \right)^{\frac{r-1}{r}} = 298K \cdot (10)^{-\frac{2}{5}} = 119K \]

\[ w = \Delta E = n \bar{c}_v \Delta T = 3R \frac{2}{2} (119K - 298K) = -2231J \]

d) Calculate the change in the Gibbs free energy when 5 moles of an ideal gas expand isothermally from an initial volume of 1 L to a final volume of 20L. Assume T=300K

Solution:
\[ dG = VdP = nRT \frac{dP}{P} \]

\[ \Delta G = \int \frac{1}{nRT} \left( \frac{P_i}{P_f} \right) dP = nRT \ln \left( \frac{P_f}{P_i} \right) = -nRT \ln \left( \frac{V_f}{V_i} \right) \]

\[ \therefore \Delta G = -(5 \text{ moles}) \left( \frac{8.31 \text{ J/moleK}}{300 \text{ K}} \right) \ln(20) = -37,342 \text{ J} \]

Part 4 (32 points): Perform one of the two multi-step calculations.

a) 18 grams of water ice at 230 K are placed in thermal contact with a large heating block maintained at a temperature of 350 K. Calculate the entropy change of the water \( \Delta S \), the enthalpy change of the water \( \Delta H \), and the energy change of the water \( \Delta E \) when 18 grams of water ice at 230 K are converted to liquid water at 350 K. Also calculate the entropy change of the heating block as a result of this process and the entropy change of the universe as a result of this process. For ice \( C_p = 37.7 \text{ J/K} \). For liquid water \( C_p = 75 \text{ J/K} \). For water \( \Delta H_{\text{fusion}} = 6.01 \text{ kJ/mole} \). Assume the density of ice is 0.92 gm/mL and approximately constant between 230K and 273K. The density of liquid water is 1 gm/mL at 273K and approximately constant up to 350K. Assume only P-V work occurs. The external pressure is 1 atm.

Solution: Designate a three-step path from water ice at T=230K to liquid water at T=350K:

\[ \text{ice}(230\text{K}) \quad \rightarrow \quad \text{water}(350\text{K}) \]

\[ \text{ice}(273\text{K}) \quad \rightarrow \quad \text{water}(273\text{K}) \]

Step 1: \( \Delta H_1 = nC_p^{\text{ice}} \Delta T = (1 \text{ mole})(37.7 \text{ J/K} \cdot \text{mole})(273 \text{K} - 230 \text{K}) = 1621 \text{J} \)

\[ \Delta S_1 = nC_p^{\text{ice}} \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = (1 \text{ mole})(37.7 \text{ J/K} \cdot \text{mole}) \ln \frac{273}{230} = 6.46 \text{J/K} \]

\[ \Delta E_1 = q_p - P_{\text{eq}} \Delta V \approx q_p = \Delta H_1 \]

Step 2: \( \Delta H_2 = (1 \text{ mole}) \Delta H_{\text{fusion}} = (1 \text{ mole})(6010 \text{ J/mole}) = 6010 \text{J} \)

\[ \Delta S_2 = \frac{\Delta H_2}{T_{\text{fusion}}} = \frac{6010 \text{J}}{273 \text{K}} = 22.0 \text{J/K} \]

\[ \Delta E_2 = q_p - P_{\text{eq}} \Delta V \Rightarrow q_p = 6010 \text{J}; \Delta V = V_{\text{liquid}} - V_{\text{ice}} \]

\[ \Delta V = 0.018L - (0.018L / 0.92) = -0.016L \]

\[ \therefore \Delta E_2 = 6010 \text{J} + (0.016L)(1 \text{ atm})(101J/L \cdot \text{atm}) = 6010.2 \text{J} \]

Step 3: \( \Delta H_3 = nC_p^{\text{liquid}} \Delta T = (1 \text{ mole})(75 \text{ J/K} \cdot \text{mole})(350 \text{K} - 273 \text{K}) = 5775 \text{J} \)

\[ \Delta S_3 = nC_p^{\text{liquid}} \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = (1 \text{ mole})(75 \text{ J/K} \cdot \text{mole}) \ln \frac{350}{273} = 18.63 \text{J/K} \]

As before \( \Delta E_3 = \Delta H_3 = 5775 \text{J} \)
Totals: \( \Delta H_{\text{water}}^R = \Delta H_1 + \Delta H_2 + \Delta H_3 = 13,406 J \)
\( \Delta S_{\text{water}}^R = \Delta S_1 + \Delta S_2 + \Delta S_3 = 47.09 J/K \)
\( \Delta E_{\text{water}}^R \approx \Delta H_{\text{water}}^R = 13,406 J \)

\( \Delta S \) for Surroundings: \( \Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{water}}^R}{T_{\text{surroundings}}} = \frac{-13,406}{350} = -38.30 J/K \)

\( \Delta S \) for Universe:
\( \Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{water}} = -38.30 J/K + 47.09 J/K = 8.79 J/K \)

b) A fuel cell is an electrochemical cell wherein a hydrocarbon (e.g. methane, propane, etc) is reacted with oxygen to form CO2 and H2O. The net chemical reaction for a methane fuel cell is: \( \text{C}_4\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \Rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \). The following thermodynamic data are available for the components of the fuel cell at T=298K.

<table>
<thead>
<tr>
<th>Chemical/Property</th>
<th>( \Delta H_0^0 ) (kJ/mole)</th>
<th>( S_0^0 ) (J/K mole)</th>
<th>( C_P^0 ) (J/K mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane (g)</td>
<td>-103.85</td>
<td>269.91</td>
<td>73.5</td>
</tr>
<tr>
<td>Oxygen (g)</td>
<td>0</td>
<td>205.138</td>
<td>29.355</td>
</tr>
<tr>
<td>Carbon Dioxide (g)</td>
<td>-393.51</td>
<td>213.74</td>
<td>37.11</td>
</tr>
<tr>
<td>Water (l)</td>
<td>-285.83</td>
<td>69.91</td>
<td>75.29</td>
</tr>
</tbody>
</table>

- Calculate the enthalpy \( \Delta H_0^0 \) and entropy \( \Delta S_0^0 \) changes for the propane fuel cell reaction at T=298K. Assume 1 mole of propane is converted.

Solution:
\( \Delta H_0^0 = 4(-285.83kJ) + 3(-393.51kJ) - (-103.85kJ) = -1143.32kJ - 1180.53kJ + 103.85kJ = -2220kJ \)
\( \Delta S_0^0 = 4(69.91kJ/K) + 3(213.74kJ/K) - 269.91kJ/K - 5(205.138kJ/K) = 279.64kJ/K + 641.22kJ/K - 269.91kJ/K - 1025.69kJ/K = -374.74kJ/K \)

- Calculate the Gibbs free energy change \( \Delta G_0^0 \) at T=298K. Will the fuel cell reaction be spontaneous at T=298K? Also, what is the maximum non-P/V work obtainable from the fuel cell? Assume one mole of propane is converted.

Solution:
\( \Delta G_0^0 = \Delta H_0^0 - T\Delta S_0^0 = -2220kJ - (298K)(-0.374kJ/K) = -2109kJ \)

The maximum non-PV work is -2109kJ

- Calculate the change in Gibbs free energy at T=400K. What is the maximum non-P/V work obtainable from the fuel cell at T=400K? Assume the heat capacities are constant between T=298K and T=400K.

Solution:
\( \Delta C_p^0 = 4(75.29kJ/K) + 3(37.11kJ/K) - 73.5kJ/K - 5(29.355kJ/K) = 301.16kJ/K + 111.33kJ/K - 73.5kJ/K - 146.78kJ/K = 192.21kJ/K \)
\[ \Delta H^0 (T_2 = 400K) = \Delta H^0 (T_1 = 298K) + \Delta C_p^0 (T_2 - T_1) \]
\[ = -2220kJ + (0.1922kJ/K)(400K - 298K) = -2200kJ \]
\[ \Delta S^0 (T_2 = 400K) = \Delta S^0 (T_1 = 298K) + \Delta C_p^0 \ln \left( \frac{T_2}{T_1} \right) \]
\[ = -374.74J/K + (192.21J/K) \ln \left( \frac{400K}{298K} \right) = -318.16J/K \]
\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 = -2200kJ - (400K)(-0.318kJ/K) = -2072.8kJ \]
The maximum non-PV work is now \(-2072.8kJ\)

- At T=298K and at T=400K, is the maximum work obtained from the fuel cell greater or less than the heat evolved by the fuel cell at constant pressure? If they are not equal, explain why they differ.

At T=298K and 400K the enthalpy changes equal the heat of reaction at constant pressure. In both cases the maximum work that the fuel cell can perform is less than the heat of reaction. This is because of the negative entropy change of the cell, which occurs because liquid water is produced and because the total moles of gas decreases from 6 to 3.