PHYSICAL CHEMISTRY I: ASSIGNMENT 1

1. A one mole sample of gas follows the equation of state given by $pV\text{m} = RT(1 + Bp)$. The gas is initially at 373 K. The gas then undergoes a Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $Cp\text{,m} = 5/2\ R$, $\mu_{JT} = 0.21$ K atm^{-1}, $B = -0.525(\text{K}/T)$ atm^{-1}. Assume that these values are constant over the temperature range involved. Derive the expression for ΔS for the gas and determine its value. [Hint: Consider the entropy as a function of temperature and pressure]

2. A three step reversible cycle consists of (i) an isothermal expansion at T_1 (ii) a constant volume (isochoric) cooling to T_2 and (iii) an adiabatic compression to the initial state. Calculate the work done in each step considering 1 mole of an ideal gas. Show that the efficiency is given by:

$$\eta = 1 - \frac{T_1 - T_2}{T_1 \ln(T_1/T_2)}$$

3. Derive the thermodynamic equation of state $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

4. Calculate the change of entropy when 200 g of ice at 0°C is added to 200 g of water at 363 K in an insulated vessel. The molecular weight of water is 18.0 gm/mole, the enthalpy of fusion for ice is 6.01 kJ/mole, and assume the heat capacity for water is 75.5 J K^{-1} mole^{-1}, independent of temperature.

5. An Otto cycle is the cycle involved in the operation of an internal combustion engine. In this case air can be considered to be the working substance that is assumed to behave like an ideal gas. The cycle consists of the following steps:
   Step I: reversible adiabatic compression from A to B;
   Step II: reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel;
   Step III: reversible adiabatic expansion from C to D;
   Step IV: reversible and constant-volume pressure decrease back to state A.

[Assume that in State A, V = 4.00 dm^3 , p = 1.00 atm, and T = 300 K; $p_C/p_B = 5$, Cp,m = 7/2 R.]

(i) On a PV diagram indicate the individual steps of the cycle marking each step
(ii) Determine the change in entropy (of the system and of the surroundings) for *Step II* of the cycle.
(iii) Evaluate the efficiency for a compression ratio of 10:1 meaning that $V_A = 10V_B$ assuming that the heat is supplied in *Step II*.