Homework 4 Problems – Entropy and Entropy Changes

1. Consider the freezing of 50.0 g of water once it is placed in the freezer compartment of a refrigerator. Assume the walls of the freezer are maintained at –10ºC. The water, initially liquid at 0.0ºC, is frozen into ice and cooled to –10ºC. Show that even though the entropy of the water decreases, the net entropy of the universe increases. You may assume that the specific heat of ice is \( c_{\text{ice}} = 2090 \, \text{J/kg}^{-1}\text{K}^{-1} \) and that the latent heat of fusion is 334 kJ/kg.

2. For this problem, you will calculate the entropy of aluminum and graphite based on experimental measurements of the heat capacity.
   a. Experimental measurements of the heat capacity of graphite over a wide range of temperatures can be fit to the formula:
      \[
      C_v = a + bT - c/T^2
      \]
      where \( a = 16.86 \, \text{J/K} \), \( b = 4.77 \times 10^{-3} \, \text{J/K}^2 \), and \( c = 8.54 \times 10^{-5} \, \text{J} \cdot \text{K} \). From this data, find a formula for the entropy of a mole of graphite as a function of temperature.
   b. Experimental measurements of the heat capacity of aluminum at low temperatures (below about 50 K) can be fit to the formula:
      \[
      C_v = aT + bT^3
      \]
      where \( C_v \) is the heat capacity of one mole of aluminum, and the constants \( a \) and \( b \) are approximately \( a = 0.00135 \, \text{J/K}^2 \) and \( b = 2.48 \times 10^{-5} \, \text{J/K}^4 \). From this data, find a formula for the entropy of a mole of aluminum as a function of temperature.
   c. In (b), note that \( C_v \to 0 \) as \( T \to 0 \). What should the entropy of aluminum become as \( T \to 0 \)? Explain why.

3. In this problem, you will derive the entropy of an ideal gas at constant particle number and examine its implications.
   a. Suppose an ideal gas evolves from a state at \( (P_1, T_1) \) to a new state of \( (P, T) \). Show that the entropy of the gas can be written as
      \[
      S(T, P) - S_1(T_1, P_1) = Nk \ln \left( \frac{T}{T_1} \right) ^{\frac{f_2}{2}} \left( \frac{P_1}{P} \right) \]
      Based on the above result, what types of spontaneous processes are permissible for an isolated ideal gas according to the 2\textsuperscript{nd} law? What types of spontaneous processes are \textbf{not} permissible according to the 2\textsuperscript{nd} law?
   b. Repeating the same procedure as in (a), find an expression for \( S(T, V) \), \( S(P, V) \), and \( S(U, V) \). Based on your results, determine what types of spontaneous processes are permissible for an isolated ideal gas according to the 2\textsuperscript{nd} law. What types of spontaneous processes are \textbf{not} permissible according to the 2\textsuperscript{nd} law?
c. Based on the results of (a) and (b), determine what types of spontaneous processes are permissible for an isolated monatomic ideal gas according to the 2nd law. What types of spontaneous processes are not permissible based on the 2nd law?

4. Imagine a narrow pipe, filled with fluid, in which the concentration of a certain type of molecule varies only along the length of the pipe in the $x$-direction, as shown below.

![Diagram of a narrow pipe with concentration variation](image)

a. By considering the flux of these particles from both directions into a short segment, derive **Fick’s Second Law**.

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$

where $D$ is the diffusion coefficient.

b. Noting the similarity to the heat equation, discuss the implications of this equation. What should the solution to Fick’s second law be? Discuss how particles spread through the pipe as time passes in terms of chemical potential and entropy. Be detailed and thorough in your explanation.

c. In analogy with the thermal conductivity, derive an approximate formula for the diffusion coefficient of an ideal gas in terms of the mean free path and the average thermal speed. How does $D$ depend on $T$, at fixed pressure?
5. In this question, you are going to examine how the temperature of dry air changes during an adiabatic process.
   a. For an adiabatic process, show that
   \[
   \frac{C_p}{R_d} \frac{dT}{T} - \frac{dP}{P} = 0
   \]
   Solve this equation to obtain
   \[
   \theta = T \left( \frac{P_0}{P} \right)^{\frac{\gamma-1}{\gamma}}
   \]
   Here, \(\theta\) is called the potential temperature. The potential temperature is defined as the temperature a gas would have if it were expanded or compressed adiabatically from its existing pressure and temperature to a standard pressure \(P_0\).
   
   b. Use the result from (a) to show that the entropy is given by
   \[
   S - S_0 = C_p \ln \left( \frac{\theta}{T_0} \right)
   \]
   This shows that an adiabatic process is also a constant-\(\theta\) process and thus, \(\theta\) is conserved for reversible, adiabatic processes.
   
   c. Show that the vertical gradient of potential temperature can be written as
   \[
   \frac{1}{\theta} \frac{\partial \theta}{\partial z} = \frac{1}{T} (\Gamma_d - \Gamma)
   \]
   where \(\Gamma_d\) is the dry adiabatic lapse rate and \(\Gamma \equiv dT/dz\) is the environmental lapse rate. Discuss the meaning of this result. Based on your derivation, what is the necessary condition for dry spontaneous convection to occur in any atmosphere? How can this expression be rephrased in terms of entropy?
   
   d. Now let’s consider a diabatic process in which the heating rate \(dQ/dt\) and the rate of working is known \(dW/dt = -P \, dV/dt\) (i.e. a conversion between the thermal and mechanical energy). Show the first law of thermodynamics can be written as
   \[
   \frac{d\theta}{dt} = \frac{\theta \dot{Q}}{C_p T}
   \]
   Discuss the meaning of this expression. How can this expression be rephrased in terms of entropy?

**Bonus [5 points]:** In the big-bang theory of the universe, the radiation energy initially confined in a small region adiabatically expands in a spherically symmetric manner. The radiation cools down as it expands. Derive a relation between the temperature \(T\) and the radius \(R\) of the spherical volume of radiation based purely on thermodynamic considerations. [Hint: Note that the radiation pressure can be written as \(P = U/3V\)]