Physics 6351 Professor Scalise
Homework Assignment #3 Spring 2025

1. You have just microwaved a cup of tea for too long and it is boiling, too hot to drink. You look around and see a punchbowl containing ice floating in water. You thoroughly mix one cup of water (no ice) from the punchbowl with your cup of tea in a thermos bottle. What is the change in entropy of the pint of liquid? Does the sign of the change make sense? Explain.

2. Suppose that

$$dU = (3 + 2xy^2)dx + (2x^2y + 3y^2z^3)dy + (3y^3z^2)dz$$

Is there a function $U(x, y, z)$ for which this is an exact differential? If not, prove it. If so, find the function U.

3. Starting from the first law $dU = TdS - PdV$, show that the equation of state for an ideal gas leads to the conclusion that U depends only on T. Proceed as follows: U could depend on T, V, and P, but because of the ideal gas equation of state (a constraint), the internal energy really only depends on two independent variables. The entropy S will also depend on these same two variables. Find the differential dS and use a Maxwell relation.

4. A gas satisfies the relation $U = \dfrac{aS^4}{NV^2}$ where a is a constant, N is the number of particles which is held fixed, V is the volume, and S is the entropy.

   (a) Derive an expression for the temperature T.

   (b) Derive an expression for the pressure P.

   (c) What is the equation of state (an equation relating P, V, T, and N) for this gas?

5. The dihydrogen molecule can exist in either of two states: parahydrogen in which the nuclear spins are antiparallel giving the molecule a ground-state total spin angular momentum of zero; and orthohydrogen in which the nuclear spins are aligned giving the molecule a total spin angular momentum of 1 $\hbar$ and z-projections of spin $s_z = +1\ \hbar$, 0, or -1 $\hbar$. The transition between the two forms occurs very slowly in the absence of a catalyst.

   (a) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in one half of the box by a partition. The pressure is P and the temperature is T. The partition is suddenly removed and the gas fills the entire box. After equilibrium is reached,

      i. What is the new pressure?

      ii. What is the new temperature?

      iii. How much heat Q was added to or removed from the gas?

      iv. What is the change in entropy?

(b) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in each half of the box by a partition. The pressure is P and the temperature is T. The partition is suddenly removed and the gas mixes in the entire box. After equilibrium is reached, what is the change in entropy?

(c) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in one half of the box by a partition. The other half of the box contains n moles of orthohydrogen. The pressure is P and the temperature is T. The partition is suddenly removed and the gas mixes in the entire box. After equilibrium is reached, what is the change in entropy?

(d) Explain why changes in entropy may be calculated even if the system is not moving through equilibrium states.

(e) At room temperature, where $k_B T$ is far above the energy difference between para- and orthohydrogen, and if you wait long enough for transitions to occur, what is the equilibrium ratio of the two forms of hydrogen.

Bonus

1. Show that the next term in Stirling's approximation is

$$N! \approx N^N e^{-N}\sqrt{2\pi N} + \frac{1}{12N} N^N e^{-N}\sqrt{2\pi N}$$