

Thermodynamics

Do two of the following three problems, each on a separate sheet (or sheets). Staple together the sheets for each problem, if using multiple sheets, but do not staple all problems together. Write at the top of the first sheet of each problem your name, subject, and problem number.

Problem 1

1. The heat capacities at constant volume and pressure are given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (1)$$

a) Use the thermodynamic identities for U and H to show that

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T} \right)_P. \quad (2)$$

b) Using these relations, show that for any thermodynamic system

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P. \quad (3)$$

c) Using your result from part (b), show that for an ideal gas

$$C_P - C_V = Nk. \quad (4)$$

Problem 2

Suppose that a cylinder contains an ideal gas which begins at a certain pressure P_0 and volume V_0 . First, the gas in the cylinder undergoes an isothermal (constant temperature) expansion to triple its initial volume. Next, the gas undergoes an isobaric (constant pressure) contraction back to its original volume. Finally, the gas undergoes an isochoric (constant volume) increase in pressure until it has returned to its original pressure.

a. Sketch a pressure vs. volume diagram for this three-step process.

b. Calculate the work done by the gas during this three-step process.

Problem 3

Consider a spin-3/2 particle which is free to exchange energy with a heat bath at constant temperature T . The spin-3/2 particle has four possible states with different values of its z -component: $s_z = +\frac{3}{2}\hbar, +\frac{1}{2}\hbar, -\frac{1}{2}\hbar, -\frac{3}{2}\hbar$.

- a) (1 pt.) A constant magnetic field B is then applied to the system. In the presence of this magnetic field, the different spin configurations s_z correspond to different energies

$$E(s_z) = -\frac{\mu_B}{\hbar}s_z B, \quad (5)$$

where μ_B is a constant. **Calculate the energies of all four spin states** in the presence of the magnetic field.

- b) (2 pt.) Because the spin is in contact with the heat bath, the probability of occupying a given particular state with energy E follows the Boltzmann distribution

$$P(E) \propto e^{-E/k_B T}. \quad (6)$$

How much less probable is it to find the system in the state $s_z = -\frac{3}{2}$ than in $s_z = +\frac{3}{2}$ (I.e., find the ratio.)

- c) (3 pt.) To make these into properly normalized probabilities, we need to find the *partition function*:

$$P(E) = \frac{1}{Z} e^{-E/k_B T} \longleftrightarrow Z = \sum_i^{\text{states}} e^{-E_i/k_B T}, \quad (7)$$

where the sum is over all possible states i of the system. **Write down the partition function Z** explicitly for the spin 3/2 particle in a magnetic field.

- d) (3 pt.) Use the Boltzmann distribution and the partition function (3) to calculate the **average value of the spin** (the net polarization)

$$\langle s_z \rangle = \sum_i^{\text{states}} (s_z)_i P(E_i). \quad (8)$$

(Hint: You can either write it all out explicitly, or you can get it from a clever derivative of Z .)

- e) (1 pt.) Use your result for the average spin polarization $\langle s_z \rangle$ to **find the average energy $\langle E \rangle$** of the system.