Problems That Require Writing

1. (4 points) It is possible for an equilibrium system to have a negative temperature $T$. Using the fact that the entropy of an isolated nonequilibrium system must increase over time, $dS/dt > 0$, show that a negative temperature subsystem is hotter than any positive temperature subsystem in that heat will always transfer from the negative temperature subsystem to the positive temperature subsystem.

2. (4 points) The entropy $S(U)$ of a certain system depends on the energy $U$ of the system according to the relation $S = a + b \ln(U)$ where $a$ and $b$ are positive constants. Calculate the heat capacity $C_V(T)$ at constant volume of this system in terms of $a$ and $b$.

3. (6 points) Consider a system consisting of two distinguishable tetrahedral dice with sides numbered from 1 to 4:

![Tetrahedral dice](image)

Define a macrostate of this system to be the sum $s$ of the digits of the two bottom faces (the faces resting on the ground), e.g. one macrostate would be $2 + 3 = 5$. List all the macrostates of this system, list all the microstates of this system, and then calculate the multiplicity $\Omega(s)$—the number of microstates consistent with a given macrostate—for each of the macrostates.

(Turn to the next page)
4. (8 points) An ideal gas with initial volume $V_0$ and initial pressure $P_0$ is cooled at constant pressure until its volume is $V_0/2$ and then the gas is expanded adiabatically back to its original volume. Determine for this two-step process whether the following quantities are positive, negative, or zero:

(a) the total change in energy $\Delta U_{total}$.
(b) the total work done on the gas $W_{total}$.
(c) the total heat $Q_{total}$ transferred to the gas.
(d) the total change in temperature $\Delta T$.

Note: do not waste precious time calculating the details of $\Delta U$, $W$, and $Q$ for the two steps, think qualitatively to get the signs directly. Also, make sure to explain briefly how you got your answers.

5. (8 points) At atmospheric pressure, water molecules H$_2$O freeze at $T \approx 270$ K, boil at $T \approx 370$ K, and, in the liquid phase, have a heat capacity at constant pressure for one mole of $C_P \approx 75$ J/K that is roughly independent of temperature.

Using your knowledge of how the heat capacity $C$ varies with temperature experimentally for solids and for gaseous H$_2$, draw a plot of the ratio $C_P(T)/R$ versus $T$ (where the gas constant $R \approx 8.3$ J/(mole·K)) that represents your prediction about how the heat capacity at constant pressure of one mole of water molecules will vary over the temperature range $0 \leq T \leq 3000$ K.

Please be sure to indicate the numerical values on the vertical axis where various plateaus occur so that your prediction can be quantitatively compared with experimental data.

You can assume that at the highest temperature of your plot, all degrees of freedom are active and that, as the temperature decreases, the degrees start to freeze out in ways that are similar to systems that you are familiar with.

The following formulas may be useful:

$$PV = N kT = nRT, \quad \Delta U = Q + W, \quad U = Nf \frac{kT}{2} = \frac{f}{2} PV, \quad W = - \int_{V_1}^{V_2} P(V) \, dV.$$

$$f = 2(3K - 6) + 3 + 3 \quad \text{or} \quad f = 2(3K - 5) + 3 + 2.$$  

$$C = \frac{Q}{\Delta T}, \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V, \quad C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P.$$  

$$S = S_1(U_1) + S_2(U_2), \quad U_1 + U_2 = U, \quad \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N}.$$