Phy 632: Problem Set 1
(Due: February 1, 2011)

1). Consider a perfect gas in boxes 1 and 2 which are thermally isolated from their surroundings but are in thermal contact with each other – recall the example of the first lecture. Assuming that the wall between the boxes can be arranged so that it is either moveable *or* permeable, prove that a perfect gas in thermodynamic equilibrium must have uniform pressure and uniform chemical potential. (*Hint:* In equilibrium, the total entropy is a maximum with respect to all the variables which determine it.)

2.) Consider a closed system for which any two of the pressure P, the volume V, and the temperature T may be chosen as the independent variables to parametrize a thermodynamic equilibrium state. Denoting the internal energy by E and the enthalpy by $H = E + PV$, prove the following:

a) The heat capacity at constant volume C_V is $C_V = \left(\frac{\partial E}{\partial T}\right)_V$ and that the heat capacity at constant pressure C_P is $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

b) $C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] = -\left(\frac{\partial P}{\partial T}\right)_V \left[P\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial E}{\partial P}\right)_T\right]$

c) $C_P - C_V = \frac{T}{V\kappa_T}\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2$ where κ_T is the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. (As an aside, note that as $\kappa_T \geq 0$ (see p.32 G.) this implies $C_P \geq C_V$.)

(Recall $C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V$ and $C_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P$.)

3). Given that the internal energy E for some system in thermodynamic equilibrium is

$$E(S, V) = \frac{AS^3}{V}\ , \qquad (1)$$

where A is a constant, determine $H(S, P)$, $F(T, V)$, and $G(T, P)$.

4). Suppose it is found experimentally for a solid that

$$\left(\frac{\partial V}{\partial T}\right)_P = a + bP + cP^2 \qquad (2)$$

for pressures in the interval $P_A \lesssim P \lesssim P_B$. Note that a, b, and c are empirically determined constants. How much will the entropy increase when the solid is compressed from a pressure P_A to P_B at constant temperature T? (*Hint:* Use Maxwell's relations!)

5). Derive an expression for the entropy of an ideal gas assuming that the specific heat (at constant volume) is independent of temperature. Note that an ideal gas obeys the equation of state $PV = Nk_BT$. Is this expression consistent with the Nernst's law? What do you think might be wrong?

6). a) For a rubber band of natural length L_0 at temperature T the applied stress τ is related to its length L via the equation of state

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] , \tag{3}$$

where k is a constant which depends on the composition and geometry of the rubber band and $L_0(T)$ is the natural length of the rubber band at T. Let $\lambda_0 = (1/L_0)(dL_0/dT)$ be the thermal expansion coefficient of rubber under zero stress. Using a Maxwell relation show that

$$\left(\frac{\partial T}{\partial L}\right)_{S,V} = \frac{T}{C_{L,V}}\left(\frac{\partial \tau}{\partial T}\right)_{L,V} \tag{4}$$

where $C_{L,V}$ is the heat capacity at constant length and volume. Determine the final temperature T when the rubber band is stretched adiabatically from L_0 at $T = T_0$ to a length L at fixed V. (You need not evaluate the final integral.)

b) Since the entropy is a function of state, we can evaluate the temperature change another way. In part a) we considered the adiabatic transition from state "0" for which the rubber band has length L_0 at temperature T_0 to state "2" for which the rubber band has length L at temperature T. Now consider a two-step process. In the first step we have a reversible isothermal expansion from state 0 to state "1" for which the length is L. In the second step we have a reversible transition from 1 to 2 at fixed length. Determine the final temperature T by demanding that the net change in entropy from $0 \to 1$ and $1 \to 2$ be zero. Can T ever be less than T_0? Explain.

7). Show that when the applied magnetic field is increased isothermally from 0 to H, the change in volume ΔV of a sample (when $|\Delta V| \ll V$) in thermodynamic equilibrium at fixed pressure P is given by

$$\left(\frac{\Delta V}{V}\right) = \frac{1}{2}H^2\{\kappa_T\chi_T - \left(\frac{\partial \chi_T}{\partial P}\right)_T\} , \tag{5}$$

where χ_T is the isothermal magnetic susceptibility

$$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T , \tag{6}$$

and M is the magnetization. To find the above result, we must assume that *i)* χ_T is taken to be independent of magnetic field and *ii)* the applied magnetic field and magnetization are *constant* over the volume of the sample. The parameter κ_T is the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,H} . \tag{7}$$

(*Hint:* In this system an infinitesimal change in the internal energy dU is given by

$$dU = TdS - PdV + Hd\mathcal{M} , \tag{8}$$

where $\mathcal{M}$ is the total magnetic moment of the sample. You would do well to consider a thermodynamic function whose natural variables were T, P, and H.)