Problem Set 2: Due 1/27

Problem 1. (10) Prove that if a differentiable relationship $F(x, y, z) = 0$ holds between three variables, the following identities are valid:

$$\left(\frac{dx}{dy}\right)_z \left(\frac{dy}{dx}\right)_z = 1 \tag{1}$$

$$\left(\frac{dx}{dy}\right)_z \left(\frac{dy}{dz}\right)_x \left(\frac{dz}{dx}\right)_y = -1 \tag{2}$$

Problem 2. (20) A *heat pump* is essentially a Carnot refrigerator, for which the heating of the high temperature reservoir is of the primary interest. Suppose a building is heated to 25^oC by a heat pump operating between the building and the underground spring at 5^oC. By how much is the energy input multiplied in this device, as compared to a simple electric heating system which converts the energy input directly into heat.

Problem 3. (30) Consider a situation where entropy $S(U, V)$ of a system with fixed number of particles is given by

$$S(U, V) = aU^2 + bUV + cV^2 \tag{3}$$

where a, b, c a some constants.

Find the the pressure and temperature by taking appropritae partial derivatives. Determine the Helmholtz and Gibbs free energies $F(T, V)$ and $G(T, p)$ as explicit functions of their arguments. Verify that

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial p}\right)_T = V \tag{4}$$

Problem 4 (40) In solids and liquids one often measures the expansion coefficient

$$\kappa_E = V^{-1} \left(\frac{\partial V}{\partial T}\right)_p \tag{5}$$

and isothermal compressibility

$$\kappa_T = -V^{-1} \left(\frac{\partial V}{\partial p}\right)_T \tag{6}$$

Show that specific heats $c_p = T\left(\frac{\partial S}{\partial T}\right)_p$ and $c_V = T\left(\frac{\partial S}{\partial T}\right)_V$ are related via

$$c_p - c_V = VT\kappa_E^2\kappa_T^{-1} \tag{7}$$

Start by regarding the entropy as a function of T and V even though these are not the "natural" variables for entropy.

Some "hints":

1) you may want to remember the existence of an equation of state ($p = p(T, V)$) even though you don't need to know what it is.

2) you may want to use a formula for differentiation under constraint. For an arbitrary $\Phi(x, y)$ and some constraint $f(x, y) = q$:

$$\left(\frac{\partial \Phi}{\partial x}\right)_q = \left(\frac{\partial \Phi}{\partial x}\right)_y + \left(\frac{\partial \Phi}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_q \tag{8}$$

3) you may want to use "Maxwell relation"

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \tag{9}$$

which follows from

$$\frac{\partial}{\partial T}\left(\frac{\partial G(T, P)}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial G(T, P)}{\partial T}\right) \tag{10}$$