CHEM 622, Spring 2009-2010 ..::HOMEWORK 1::.. Due: 10 March

1. (5 points each) `LEGENDRE TRANSFORMS`

(a) Let $\alpha > 1$ and $\beta > 1$. Show that the Legendre transform of $f(x) = x^\alpha/\alpha$ is $g(p) = p^\beta/\beta$ where $\alpha^{-1} + \beta^{-1} = 1$.

(b) In thermodynamics the natural variables of the energy function are S, V, and N, i.e. $E := E(S, V, N)$. Through Legendre transformation(s) of $E(S, V, N)$ one can obtain different thermodynamic functions such as enthalpy $H(S, p, N)$ and Helmholtz free energy $A(T, V, N)$. What is the total number of all possible *distinct* thermodynamic functions that can be obtained formally from $E(S, V, N)$ by way of Legendre transformation?

(c) The grand potential $\Phi := \Phi(T, p, \mu)$ is obtained from energy $E(S, V, N)$ by way of Legendre transforms. Evaluate the total differential $\mathrm{d}\Phi$ and partial derivatives of Φ with respect to its natural variables.

2. (10 points each) `REDUCTION OF THERMODYNAMIC EXPRESSIONS:` Prove the following equations by exploiting Maxwell and other relations on partial and total derivatives.

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = \frac{\alpha T}{\kappa_T} - p \tag{1}$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,N} = (1 - \alpha T)V \tag{2}$$

$$\left(\frac{\partial C_V}{\partial V}\right)_{T,N} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \tag{3}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_{T,N} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{4}$$

$$c_p - c_v = \frac{\alpha^2 T v}{\kappa_T} \tag{5}$$

where $c_p := C_p/N$ and $c_v := C_V/N$.

3. (5 points) Evaluate the right hand sides of equations (1–5) in question (2) for an ideal gas satisfying the equation of state $pV = NRT$.

4. (10 points) Evaluate the right hand sides of equations (1–5) in question (2) for a van der Waals fluid obeying the following equation of state.

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NRT$$

Here a and b are positive constants specific for each fluid.

5. (20 points) Reduce the following expression.

$$\left(\frac{\partial S}{\partial V}\right)_H$$