PHYSICAL CHEMISTRY I Mid-Term Exam 2 (May 28th. Spring 2009)

1. (a) (10 pt) For a particular system it is found that

$$\begin{aligned} u &= \frac{3}{2}Pv \\ P &= AvT^4 \end{aligned} \tag{1}$$

Find the fundamental equation of this system in entropy representation [i.e. obtain the entropy of this system as a function of u and v. $s = s(u, v)$]

(b) (10 pt) Show that

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -Tv\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P\right], \tag{2}$$

and evaluate this value $(\partial c_p/\partial P)$ for an ideal gas.

(c) (10 pt) A particular system obeys the relation

$$u = A\frac{e^{s/R}}{v^2} \tag{3}$$

N moles of this substance, initially at temperature T_0 and pressure P_0 are expanded isentropically ($s =$ constnat) until the pressure is halved. What is the final temperature?

2. A certain system is found to have a Helmholtz free energy given by

$$F(T, V, N) = F_0 - NRT\log\left[\frac{T^{3/2}V}{N}\right] \tag{4}$$

where F_0 is a constant.

(a) Find the molar heat capacity at constant volume c_v (10 pt)

(b) Perform a Legendre transform and obtain the Gibbs free energy $G(T, P, N)$ of the system (10 pt).

3. A mole of an "ideal gas" system undergoes an expansion.

(a) If this expansion is a *reversible* "isothermal expansion" from volume V_1 to $2V_1$, then

(i) what is the change in entropy of the gas system?

(ii) What is the change in entropy of the whole universe (universe = system + reservior) ? (10 pt)

(b) Suppose the expansion is *free expansion* from V_1 to $2V_1$ then

(i) what is the change in entropy of the gas system ?

(ii) What is the change in the entropy of the whole universe ? (10 pt)

4. Consider the free expansion process for a mole of real gas system from V_0 to $2V_0$. The temperature change with volume as

$$\Delta T = T_f - T_i = \int_{V_0}^{2V_0} \left(\frac{\partial T}{\partial V}\right)_{U,N} dV \tag{5}$$

(a) Show that (15 pt)

$$\left(\frac{\partial T}{\partial V}\right)_{U,N} = \frac{1}{C_v}\left[P - \frac{T\alpha}{\kappa_T}\right] \tag{6}$$

(b) If this the gas system is made of a mole of "van der Waals fluid", whose mechanical equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{7}$$

calculate T_f. Express you answer using V_0, a, R, C_v and T_i. Does temperature increase or decrease upon free expansion ? (15 pt)