679 Homework Set # 5

1. Reduce the following partial derivatives (you may make use of intermediate results derived in class):
   a. $\left(\frac{\partial S}{\partial P}\right)_T$
   b. $\left(\frac{\partial P}{\partial S}\right)_V$
   c. $\left(\frac{\partial A}{\partial V}\right)_T$
   d. $\left(\frac{\partial H}{\partial P}\right)_T$
   e. $\left(\frac{\partial U}{\partial T}\right)_P$

2. The volume derivative of the energy of a fluid, $\left(\frac{\partial U}{\partial V}\right)_T$, has units of pressure and is often referred to as the fluid's internal pressure. Show that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha_p}{\kappa_T}\right) - P$.

3. Show that the derivatives of $\alpha_p$ and $\kappa_T$ are related, so that $\left(\frac{\partial \alpha_p}{\partial P}\right)_T = -\left(\frac{\partial \kappa_T}{\partial T}\right)_P$.

4. Show that $(\partial C_P / \partial P)_T = -T(\partial^2 V / \partial T^2)_V$, (where $C_P$ is the total, not molar, heat capacity of the system), and reduce the right-hand-side to an expression containing $\alpha_p$ and $(\partial \alpha_p / \partial T)_P$.

5. Show that $(\partial C_V / \partial V)_T = T(\partial^2 P / \partial T^2)_V$, (where $C_V$ is the total, not molar, heat capacity of the system), and reduce the right-hand-side to an expression containing the quantity $(\alpha_p/k_P)$, and its derivatives with respect to temperature and pressure.

6. The partial molar partial molar volume, $\bar{V}$, of a solute $(N)$ in a solvent $(N_S)$ is defined as $\bar{V} = (\partial V / \partial N)_{T,P,N\neq N_S}$. Show that $(\partial \bar{V} / \partial T)_V$ can also be expressed as $(\partial \bar{V} / \partial T)_P$ plus an additional term that is proportional to the pressure derivative of $\bar{V}$, $(\partial \bar{V} / \partial P)_T$, and identify the missing constant of proportionality (and reduce it).

7. The pressure change induced by adding a solute molecule to a system that is held at constant volume is defined as, $\bar{P} = (\partial P / \partial N)_{T,V,N\neq N_S}$. Show that this pressure change is related to the partial molar volume of the same solute as follows.

$$\bar{P} = \frac{\bar{V}}{V \kappa_p}$$

8. Show that the pressure dependence of the partial molar energy, $\bar{U} = (\partial U / \partial N)_{T,P,N\neq N_S}$, is related to the temperature and pressure derivatives of the partial molar volume as follows.

$$\left(\frac{\partial \bar{U}}{\partial P}\right)_T = -T\left(\frac{\partial \bar{V}}{\partial T}\right)_P - P\left(\frac{\partial \bar{V}}{\partial P}\right)_T$$

There will be an in-class exam on Oct. 20th.
This exam will cover material in the first five homework sets.