Chemistry 230
Problem Set # 10 — 11/1/99

Recommended Problems: Chapt. 8: 1, 3, 5, 7, 11, 12, 14, 15, 19-23; 31
Chapt. 10: 43-48
Chapt. 11: 26-29

1. The vapor pressure of water at 25˚C is 23.756 torr. Calculate ΔG°_{298} for the process, $H_2O(l) \rightarrow H_2O(g)$: (a) First assuming the vapor is an ideal gas, and (b) next, using the van der Waals equation for the vapor. In the latter case, use the results from Problem 8.15a along with data from Section 8.4 to correct for nonideality. Finally, (c) compare both results with a value calculated from tabulated data in the Appendix.

2. (a) Evaluate the van der Waals *a* and *b* for CO_2 from the critical data given in Table 8.1. (b) Use these values together with the results of Problem 8.15a to determine (*i*) $H_{m,id} - H_m$, (*ii*) $S_{m,id} - S_m$, and (*iii*) $G_{m,id} - G_m$ for CO_2 at 25˚C and 1 bar.

3. The following molar volumes were measured for CO_2 at 333 K:

P(atm)	13.01	35.42	53.65	74.68	85.35
V_m(cm^3/mol)	2000	666.7	400.0	250.0	200.0

   (a) Calculate the fugacity *f* and fugacity coefficient φ at 333 K and (*i*) 40.0 atm and (*ii*) 90.0 atm.
   (b) Compare your results with estimates obtained using Fig. 10.11. (See Table 8.1 for critical data.)
   (c) In a final comparison, use the van der Waals equation, with *a* and *b* parameters obtained in Problem 2 above, to estimate *f* and φ at the temperatures and pressures given in (a).

4. The following data are obtained for the reaction, $NiO(s) + CO(g) \rightleftarrows Ni(s) + CO_2(g)$:

T(K)	936	1027	1125
K°	4.54×10^3	2.55×10^3	1.58×10^3

   (a) Calculate ΔG°, ΔH°, and ΔS° for this reaction at 1000 K.
   (b) Is ΔC_P for the reaction positive, negative, or indeterminate?
   (c) Would an atmosphere of 20% CO_2, 5% CO, and 75% N_2 oxidize Ni at 1000 K?

5. Problem 11.31 in Levine deals with the reaction, $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$. In part (b) K° is estimated to be 4.5 at 1273 K. The densities of $CaCO_3(s)$ and $CaO(s)$ are 2.71 g/cm^3 and 3.38 g/cm^3, respectively. Calculate the equilibrium pressure of CO_2 at 1273 K in the presence of 1111 atm of Ar, assumed to be inert with respect to the reactants and products. [**Hint:** The activities of the solids can no longer be taken as unity. Also, the fugacity of $CO_2(g)$ needs to be taken into account; use the Lewis-Randall rule and the method of Problem 3b above to do so.]