## Chemistry 230 <br> Problem Set \# 8 - 10/18/99

Recommended Problems: $\quad$ Chapt. 6: 1-6, 18, 28-33, 36, 37, 40, 41, 48

1. Use data in the Appendix to calculate the conventional chemical potential for $\mathrm{NH}_{3}(g)$ at 325 K and 2.65 bar pressure. [Use the convention that $H^{\circ}{ }_{\mathrm{m}, 298} \equiv 0.0$ for elements in their standard states at $25^{\circ} \mathrm{C}$.]
2. Consider the reaction, $\mathrm{CO}(g)+1 / 2 \mathrm{O}_{2}(g) \rightleftarrows \mathrm{CO}_{2}(g)$. (a) Use data in the Appendix and the expression for $\Delta H^{\circ}$ found in Section 5.5 to obtain an expression for $\ln K^{\circ} P(T)$ valid from 300 to 2000 K . (b) Use this expression to calculate $K^{\circ}$ at 1500 K .
3. Many reactions involve dissociation of a starting substance into products. The simplest case is

$$
\mathrm{A}(g) \leftrightarrow 2 \mathrm{~B}(g)
$$

If we start with $n_{0}$ of A , we define the degree of dissociation $\alpha$ as that fraction of $n_{0}$ that has dissociated when equilibrium is reached. Obtain an expression for $\alpha$ as a function of $K^{\circ}{ }_{P}$ and $P$.
Dissociation reactions are almost always endothermic. How will changes in $P$ and $T$ affect $\alpha$ ?
4. Do Problem 6.9 , except make the temperature 500 K , and do not neglect the $T$-dependence of $\Delta H^{\circ}$. Also, calculate the degree of dissociation $\alpha$ under conditions where (a) the total pressure is maintained at 0.900 bar, and (b) where the pressure would be 0.900 bar if the gas remained entirely $\mathrm{PCl}_{5}$, but where the volume is held constant (thus yielding increased $P$ at equilibrium). [Hint: The $T$-dependence of $\Delta H^{\circ}$ can be accommodated through Eq. 5.18, as discussed on p. 172. For the $\alpha$ calculations, you may need to re-express $\alpha$ for the reaction, $\mathrm{A}(g) \leftrightarrow \mathrm{B}(g)+\mathrm{C}(g)$, since this form is appropriate for the $\mathrm{PCl}_{5}$ dissociation.]
5. Problem 6.44 in Levine. (d) Also calculate $K^{\circ}{ }_{P}$ for the reaction at 500 K and determine the equilibrium pressures of the three gases. (e) Then verify that these values indeed minimize $G$ for the reaction.
6. Repeat the previous problem, but now hold the volume constant, and calculate the Helmholz free energy $A$ as a function of $\xi$. For comparison with the previous results, make the initial pressure 4.00 bar (as in problem 6.44). Determine the equilibrium pressures and verify that these minimize $A$ for the reaction.

