Chemistry 410B **Exam 5** **Spring 2008**

Solutions

1. Calculate ΔG for the isothermal expansion of 2.00 mol of an ideal gas from 1.00 L to 20.0 L at 298 K. **Solution:** Because the process is isothermal, $\Delta T = 0$, and this greatly simplifies ΔG:

$$\begin{aligned}
G &= E + PV - TS \\
\Delta G &= \Delta E + \Delta(PV) - \Delta(TS) \\
&= C_V \Delta T + nR\Delta T - T\Delta S = 0 + 0 - T\left(nR\ln\frac{V_f}{V_i}\right) \\
&= -(298\text{ K})\left[(2.00\text{ mol})(8.3145\text{ J K}^{-1}\text{ mol}^{-1})\ln\frac{20.0}{1.00}\right] = \boxed{-14.8\text{ kJ}}.
\end{aligned}$$

2. The vapor pressure of ethanol at 298 K is 0.320 bar, and the normal boiling point is 351 K. Find the standard enthalpy of vaporization for ethanol. **Solution:**

$$\begin{aligned}
\ln P(\text{bar}) &= \frac{\Delta_{\text{vap}}H_m^\ominus}{R}\left(\frac{1}{T_b^\ominus} - \frac{1}{T}\right) \\
\Delta_{\text{vap}}H_m^\ominus &= R\ln P(\text{bar})\left(\frac{1}{T_b^\ominus} - \frac{1}{T}\right)^{-1} \\
&= (8.3145\text{ J K}^{-1}\text{ mol}^{-1})(\ln 0.320)\left(\frac{1}{351\text{ K}} - \frac{1}{298\text{ K}}\right)^{-1} \\
&= 18.7 \cdot 10^3\text{ J mol}^{-1} = \boxed{18.7\text{ kJ mol}^{-1}}.
\end{aligned}$$

3. We transfer 50.0 kJ of heat into a 36.0 g sample of liquid water initially at 350 K, so that all the water heats up to the boiling point and some evaporates, all at 1 bar. What is the mass of water remaining as liquid at the end of this process? $C_{Pm}(l) = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$. **Solution:**

$$\begin{aligned}
q &= \Delta_{\text{heat}}H + \Delta_{\text{vap}}H \\
&= n_{\text{tot}}C_{Pm}(l)\,\Delta T + n_{\text{gas}}\Delta_{\text{vap}}H_m^\ominus \\
n_{\text{gas}} &= \frac{1}{\Delta_{\text{vap}}H_m^\ominus}\left[q - n_{\text{tot}}C_{Pm}(l)\,\Delta T\right] \\
&= \frac{1}{40.65\text{ kJ mol}^{-1}}\left[50\text{ kJ} - \frac{36.0\text{ g}}{18.0\text{ g mol}^{-1}}(75.3\text{ J K}^{-1}\text{ mol}^{-1})(10^{-3}\text{ kJ/ J})(373\text{ K} - 350\text{ K})\right] \\
&= 1.14\text{ mol} \\
n_{\text{liq}} &= n_{\text{tot}} - n_{\text{gas}} = 0.86\text{ mol} \\
m_{\text{liq}} &= (0.86\text{ mol})(18.0\text{ g mol}^{-1}) = \boxed{15.5\,\text{g}}.
\end{aligned}$$

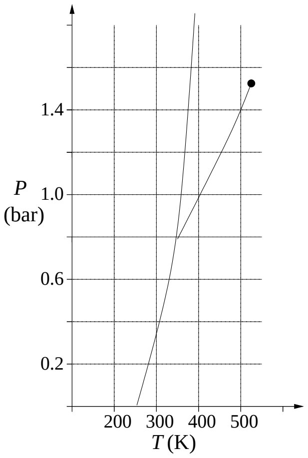
4. A sample contains a mixture of water and ammonia at a pressure and temperature such that the water is present in three phases (solid, liquid and gas) but the ammonia

exists only as liquid and gas. Calculate how many degrees of freedom this system has, using the same method used to obtain the Gibbs phase rule. **Solution:** The constraining equations we have would be:

$$\begin{aligned} \mu_{H_2O(g)} &= \mu_{H_2O(l)} & \mu_{H_2O(l)} &= \mu_{H_2O(s)} \\ \mu_{NH_3(g)} &= \mu_{NH_3(l)} & X_{NH_3(s)} &= 1 \\ X_{H_2O(l)} + X_{NH_3(l)} &= 1 & X_{H_2O(g)} + X_{NH_3(g)} &= 1 \end{aligned}$$

where the variables are the 5 mole fractions given above plus P and T. That's a total of 6 equations and 7 variables, leaving $7 - 6 = \boxed{1}$ degree of freedom.

5. For the phase diagram sketched below:



(a) What is the maximum pressure at which sublimation occurs? **Solution:** That would be at the triple point, roughly $P = \boxed{0.8\,\text{bar}}$.

(b) What is $T_b^\ominus$? **Solution:** That's T where the liquid/gas phase boundary reaches $P = 1.0$ bar, roughly $T_b^\ominus = \boxed{400\,\text{K}}$.

(c) Estimate $\Delta_{\text{vap}} H_m^\ominus$ for the substance. **Solution:** From the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V},$$

where dP/dT is the slope of the liquid/gas phase boundary and $\Delta_{\text{vap}} V \approx V_{\text{gas}} = nRT/P$. So we can solve for $\Delta_{\text{vap}} H_m^\ominus$ as follows:

$$\begin{aligned} \Delta_{\text{vap}} H_m^\ominus &= T_b^\ominus \Delta_{\text{vap}} V_m \frac{dP}{dT} \approx T_b^\ominus \left(\frac{R T_b^\ominus}{P} \right) \frac{dP}{dT} \\ &= (400\text{ K}) \left(\frac{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(400\text{ K})}{(1\text{ bar})(10^5\,\text{Pa}\,\text{bar}^{-1})} \right) \frac{[(1.0 - 0.8)\text{ bar}](10^5\,\text{Pa}\,\text{bar}^{-1})}{(400 - 350)\text{ K}} \\ &= 5320\text{ J mol}^{-1} = \boxed{5.3\text{ kJ mol}^{-1}}. \end{aligned}$$