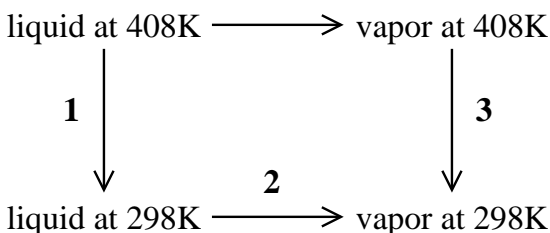


# Chemistry 2720 Fall 2001 Assignment 5 Solutions

1. (a) Vaporization is the process  $\text{TiCl}_{4(l)} \rightarrow \text{TiCl}_{4(g)}$ . To calculate the enthalpy of vaporization at the boiling point, we create a thermodynamic cycle:



The overall enthalpy change will just be the sums of the enthalpy changes for steps 1, 2 and 3.  $\Delta\bar{H}_2$  is easy: It's just the standard enthalpy change for the reaction:

$$\Delta\bar{H}_2 = \Delta\bar{H}_{f(g)}^\circ - \Delta\bar{H}_{f(l)}^\circ = -763.2 - (-804.16) \text{ kJ/mol} = 41.0 \text{ kJ/mol}.$$

The other two steps are cooling and heating steps. The enthalpy change for each is

$$\begin{aligned}
 \Delta\bar{H} &= \int_{T_i}^{T_f} \bar{C}_P dT \\
 &= \int_{T_i}^{T_f} (A + BT + CT^2 + DT^3 + E/T^2) dT \\
 &= \left[ AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 + \frac{1}{4}DT^4 - E/T \right]_{T_i}^{T_f}.
 \end{aligned}$$

In step 1, the heat capacity parameters are those of the liquid,  $T_i = 408 \text{ K}$  and  $T_f = 298 \text{ K}$ .

$$\begin{aligned}
 \Delta\bar{H}_1 &= 143.048(298 - 408) + \frac{1}{2}(7.600362 \times 10^{-3})(298^2 - 408^2) \\
 &\quad + \frac{1}{3}(1.530575 \times 10^{-6})(298^3 - 408^3) + \frac{1}{4}(-5.38376 \times 10^{-10})(298^4 - 408^4) \\
 &\quad - (-20638) \left( \frac{1}{298} - \frac{1}{408} \right) \\
 &= -16.0 \text{ kJ/mol}.
 \end{aligned}$$

In step 3, the vapor is being warmed from  $T_i = 298 \text{ K}$  to  $T_f = 408 \text{ K}$ .

$$\begin{aligned}\Delta\bar{H}_3 &= 106.8573(408 - 298) + \frac{1}{2}(1.049482 \times 10^{-3})(408^2 - 298^2) \\ &\quad + \frac{1}{3}(-2.843 \times 10^{-7})(408^3 - 298^3) + \frac{1}{4}(2.4257 \times 10^{-11})(408^4 - 298^4) \\ &\quad - (-1043516) \left( \frac{1}{408} - \frac{1}{298} \right) \\ &= 10.8 \text{ kJ/mol.}\end{aligned}$$

The enthalpy of vaporization at the boiling point is therefore

$$\Delta\bar{H}_{\text{vap}} = \Delta\bar{H}_1 + \Delta\bar{H}_2 + \Delta\bar{H}_3 = 35.7 \text{ kJ/mol.}$$

(b) The entropy change is defined by

$$\Delta\bar{S} = \int \frac{dq_{\text{rev}}}{T}.$$

A phase change at the phase transition temperature is a reversible isothermal process, therefore

$$\Delta\bar{S}_{\text{vap}} = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta\bar{H}_{\text{vap}}}{T} = \frac{35700 \text{ J/mol}}{408 \text{ K}} = 87.5 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Entropies of vaporization of  $80\text{--}90 \text{ J K}^{-1} \text{ mol}^{-1}$  are extremely common. This observation is known as Trouton's rule. The most important group of substances which violate this rule are those which form strong hydrogen bonds. For other substances, the rule is generally so closely followed that it is sometimes used to estimate the enthalpy of vaporization given the boiling point.

2. (a) This is a straightforward heat balance problem. We need the number of moles of iron:

$$n_{\text{Fe}} = \frac{20 \text{ g}}{55.85 \text{ g/mol}} = 0.36 \text{ mol.}$$

$$\begin{aligned}q = 0 &= n_{\text{Fe}}\bar{C}_{P(\text{Fe})}\Delta T_{\text{Fe}} + m_{\text{H}_2\text{O}}\bar{C}_{P(\text{H}_2\text{O})}\Delta T_{\text{H}_2\text{O}} \\ &= (0.36 \text{ mol})(25.1 \text{ J K}^{-1} \text{ mol}^{-1})(T_f - 85^\circ\text{C}) \\ &\quad + (80 \text{ g})(4.184 \text{ J K}^{-1} \text{ g}^{-1})(T_f - 4^\circ\text{C}). \\ \therefore 344T_f &= 2103. \\ \therefore T_f &= 6^\circ\text{C}.\end{aligned}$$

(b) The entropy change for the iron is

$$\begin{aligned}\Delta S_{\text{Fe}} &= \int \frac{dq_{\text{rev}}}{T} = \int_{358\text{K}}^{279\text{K}} \frac{n_{\text{Fe}} \bar{C}_P(\text{Fe}) dT}{T} \\ &= (0.36 \text{ mol})(25.1 \text{ JK}^{-1} \text{ mol}^{-1}) \ln \left( \frac{279}{358} \right) \\ &= -2.24 \text{ J/K}.\end{aligned}$$

Note the use of Kelvin temperatures in this calculation. For the water, we have

$$\begin{aligned}\Delta S_{\text{H}_2\text{O}} &= \int \frac{dq_{\text{rev}}}{T} = \int_{277\text{K}}^{279\text{K}} \frac{m_{\text{H}_2\text{O}} \tilde{C}_P(\text{H}_2\text{O}) dT}{T} \\ &= (80 \text{ g})(4.184 \text{ JK}^{-1} \text{ g}^{-1}) \ln \left( \frac{279}{277} \right) \\ &= 2.41 \text{ J/K}.\end{aligned}$$

The overall entropy change is therefore

$$\Delta S = \Delta S_{\text{Fe}} + \Delta S_{\text{H}_2\text{O}} = 0.17 \text{ J/K}.$$

The second law says that that entropy change for a spontaneous adiabatic process should be positive. We know that temperature equilibration is a spontaneous process. The positive entropy change calculated is therefore in accord with the second law of thermodynamics.

3. We should be able to calculate the entropy of water at any temperature given the entropy at one temperature and the heat capacities. One way to do this problem is to start with the entropy at 0°C and to see if it is consistent with one of the other two entropies. If it is, then it is correct, along with the other entropy which can be predicted from the entropy at the freezing point. If we can't predict either of the other two values, then the entropy at 0°C is the one that is wrong. In principle, we should be able to calculate the entropy of liquid water at temperature  $T$  by

$$\bar{S}_{\text{H}_2\text{O}}(T) = \bar{S}_{\text{H}_2\text{O}}(0^\circ\text{C}) + \bar{C}_P \int_{273.15\text{K}}^T \frac{dT'}{T'} = \bar{S}_{\text{H}_2\text{O}}(0^\circ\text{C}) + \bar{C}_P \ln \left( \frac{T}{273.15\text{K}} \right).$$

The specific heat capacity of liquid water is  $75.40 \text{ JK}^{-1} \text{ mol}^{-1}$ . According to appendix C, the entropy of liquid water at 0°C is  $63.2 \text{ JK}^{-1} \text{ mol}^{-1}$ . The entropy at 25°C should therefore be  $69.8 \text{ JK}^{-1} \text{ mol}^{-1}$ . The values of the entropy at 0 and 25°C are therefore inconsistent: One of them must be wrong. If we calculate the entropy at 100°C starting from the entropy at 0, we get  $86.7 \text{ JK}^{-1} \text{ mol}^{-1}$ . This is reasonably close to the value given in the appendix. The small difference is attributable to the fact that the heat capacity isn't quite constant. The value of the entropy at 25°C is therefore wrong.

This is not at all the only way to do this problem. We could start from ice and show that the entropy of liquid water is roughly consistent with the entropy of ice given in the appendix, which would of course reinforce our belief that this value is correct. Here is the relevant calculation:

$$\begin{aligned}\Delta\bar{S}_{\text{melt}} &= \frac{\Delta\bar{H}_{\text{melt}}}{T_{\text{melt}}} = 21.99\text{JK}^{-1}\text{mol}^{-1}. \\ \bar{S}_{\text{l}}(0^\circ\text{C}) &= \bar{S}_{\text{s}}(0^\circ\text{C}) + \Delta\bar{S}_{\text{melt}} = 63.0\text{JK}^{-1}\text{mol}^{-1}.\end{aligned}$$

The latter value is within experimental error of the value given in the table. We could then show (as we did above) that the value of the entropy at  $25^\circ\text{C}$  is wrong. We might then close the demonstration by showing that the value of the entropy of liquid water at  $100^\circ\text{C}$  is consistent with the entropy of steam by a calculation analogous to that shown above.