Chemistry 2000 Fall 2017 Test 2 Version B Solutions

1. Start with a balanced reaction:

$$\mathrm{CH_{4(g)} + 2\,O_{2(g)} \longrightarrow CO_{2(g)} + 2\,H_2O}$$

   (a) liquid water:

$$\begin{aligned}\Delta_r S^\circ &= S^\circ(\mathrm{CO_2}) + 2S^\circ(\mathrm{H_2O,l}) - [S^\circ(\mathrm{CH_4}) + 2S^\circ(\mathrm{O_2})]\\ &= 213.7 + 2(69.940) - [186.1 + 2(205.0)]\ \mathrm{J\,K^{-1}mol^{-1}}\\ &= -242.5\,\mathrm{J\,K^{-1}mol^{-1}}.\end{aligned}$$

   Note that there is **one** decimal place in the answer because some of the entropies only have **one** decimal place, and we're adding/subtracting values here.

   (b) water vapor:

$$\begin{aligned}\Delta_r S^\circ &= S^\circ(\mathrm{CO_2}) + 2S^\circ(\mathrm{H_2O,g}) - [S^\circ(\mathrm{CH_4}) + 2S^\circ(\mathrm{O_2})]\\ &= 213.7 + 2(188.72) - [186.1 + 2(205.0)]\ \mathrm{J\,K^{-1}mol^{-1}}\\ &= -5.0\,\mathrm{J\,K^{-1}mol^{-1}}.\end{aligned}$$

   In (a), the reaction converts 3 gas molecules to 1, and 2 molecules in the liquid state. Because molecules in the liquid state have far less entropy than gaseous molecules, we get a large decrease in entropy. In (b) on the other hand, the number of gas molecules is the same on the reactant and product sides, so there is a relatively small change in the entropy. It turns out there is still a decrease in entropy, but it could equally well have been a small increase.

2. For a thermodynamically allowed reaction, $\Delta_r G = \Delta_r H - T\Delta_r S < 0$. In this case, $\Delta_r H < 0$ and $-T\Delta_r S < 0$, so $\Delta_r G$ is always negative. Accordingly, the reaction is allowed at any temperature.

3. (a) We need to read the temperature and logarithm of the pressure from the diagram. If you're going to do this by hand, it helps a lot to draw lines from the triple point to the coordinate axes, drawing them as nearly perpendicular to the axes as possible (figure 1). If we do this, we find (approximately)

$$\begin{aligned}T &= 401\,K\\ \ln p &= 3.5\end{aligned}$$

   From this last datum, we get $p = e^{3/5} = 33\,\mathrm{Pa}$. Your answers might differ slightly depending on how well we were all able to draw lines through the triple point perpendicular to the coordinate axes.

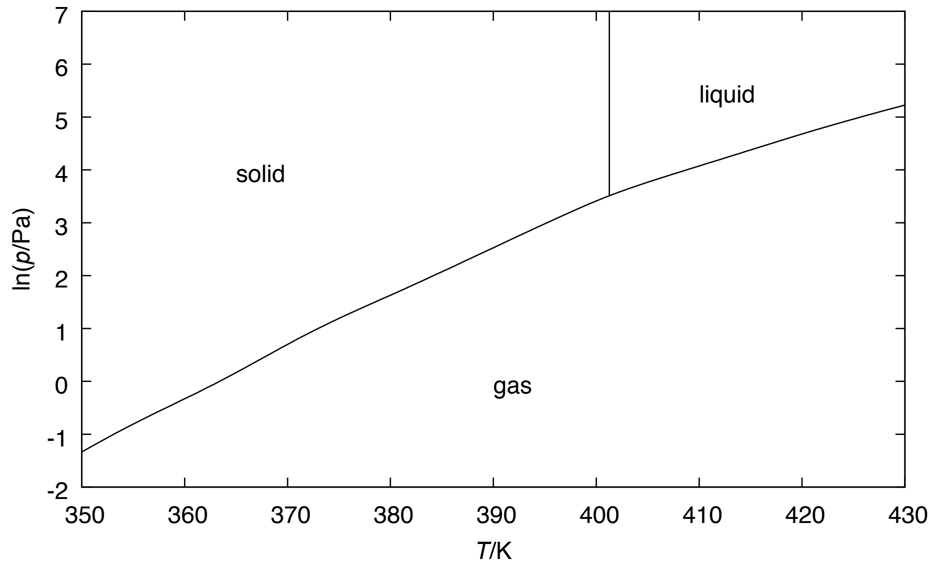

Figure 1: Phase diagram of nicotinamide, with lines added to help us read the axes.

(b) Yes. Note how vertical the solid-liquid coexistence (freezing) curve is in this phase diagram. Thus, pressure has very little effect on the freezing point, so it should be a good calibration point for a thermometer.

4. Vaporization refers to the process l $\rightarrow$ g. The equilibrium constant is $K = a_g/a_l = p/p^\circ$ since we are dealing with a pure liquid. We will be using the formula

$$\ln\left(\frac{K_2}{K_1}\right) = \ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}} H_m^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

We will be solving this equation for the enthalpy:

$$\Delta_{\text{vap}} H^\circ = \frac{R\ln(p_2/p_1)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}.$$

Label the points in the table so we don't lose track of what we're doing:

	T/K	p/bar
1:	347.78	8.5×10^{-6}
2:	377.39	1.496×10^{-4}

Now we just have to substitute everything into the equation:

$$\begin{aligned}\Delta_{\text{vap}}H^\circ &= \frac{(8.314\,460\,\text{J K}^{-1}\text{mol}^{-1})\ln\left(\dfrac{1.496\times 10^{-4}}{8.5\times 10^{-6}}\right)}{\dfrac{1}{347.78}-\dfrac{1}{377.39\,\text{K}}}\\ &= 105\,695\,\text{J mol}^{-1}\\ &\equiv 106\,\text{kJ mol}^{-1}.\end{aligned}$$

5. (a) The melting point is $T = -11.5 + 273.15\,\text{K} = 259.8\,\text{K}$. Calculating $\Delta_{\text{fus}}S$ is a straightforward application of $\Delta S = q_{\text{rev}}/T$:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} = \frac{8412\,\text{J mol}^{-1}}{259.8\,\text{K}} = 32.38\,\text{J K}^{-1}\text{mol}^{-1}.$$

(b) The principle to be applied here is that $\Delta S_{\text{universe}}$ must be positive for a process that can occur. If melting absorbs $8412\,\text{J mol}^{-1}$, then this heat must come from the surroundings. For the surroundings then, we have $q_{\text{rev}} = -8412\,\text{J mol}^{-1}$.

$$\begin{aligned}\Delta S_{\text{surr}} &= \frac{q_{\text{rev}}}{T} = \frac{-8412\,\text{J mol}^{-1}}{278\,\text{K}} = -30.2\,\text{J K}^{-1}\text{mol}^{-1}.\\ \therefore \Delta S_{\text{universe}} &= \Delta S_{\text{surr}} + \Delta_{\text{fus}}S\\ &= -30.2 + 32.38\,\text{J K}^{-1}\text{mol}^{-1}\\ &= 2.1\,\text{J K}^{-1}\text{mol}^{-1} > 0.\end{aligned}$$

Melting of hydrogen cyanide in a room at 5 °C is therefore allowed. (That is *will* happen as opposed to simply being allowed relies on the fact that melting does not require nucleation, but we didn't talk about that.)

There is a second possible approach, but it requires that you bend the definition of free energy a bit. Nevertheless, I gave this approach full marks for at least showing that the students who used it had a reasonable understanding of the criteria for thermodynamic feasibility. Here it is: We have $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}S$. Using the fact that these two quantities vary little with temperature, we can calculate $\Delta_{\text{fus}}G$ at 0 °C:

$$\begin{aligned}\Delta_{\text{fus}}G &= \Delta_{\text{fus}}H - T\Delta_{\text{fus}}S\\ &= 8412\,\text{J mol}^{-1} - (278\,\text{K})(32.38\,\text{J K}^{-1}\text{mol}^{-1})\\ &= -596\,\text{J mol}^{-1} < 0.\end{aligned}$$

Since Δ_{fus} is negative, melting is allowed. Here's the problem with this: When we derived the condition $\Delta_r G < 0$, we assumed that the system and surroundings were at the same temperature. This is not the case for melting, where the system stays at the melting temperature until all of the solid has melted. This is therefore an illegitimate use of ΔG. Having said that, you can "fix" the derivation so that T is the temperature of the surroundings, and not of the system, but then the quantity you have is not quite our usual ΔG.

6. (a) The solubility product is the equilibrium constant for the reaction

$$Ag_2SO_{4(s)} \rightleftharpoons 2\,Ag^+_{(aq)} + SO^{2-}_{4(aq)}.$$

For this reaction, we have the equilibrium expression

$$K_{sp} = (a_{Ag^+})^2 \left(a_{SO_4^{2-}}\right).$$

If the solubility (the number of moles of silver sulfate that dissolve per litre of water) is s, then we have (neglecting c°, which has the value 1 mol/L) $a_{Ag^+} = 2s$ and $a_{SO_4^{2-}} = s$. Therefore

$$K_{sp} = (2s)^2 s = 4s^3.$$
$$\therefore s^3 = K_{sp}/4 = (1.19 \times 10^{-5})/4 = 2.98 \times 10^{-6}.$$
$$\therefore s = \left(2.98 \times 10^{-6}\right)^{1/3} = 1.44 \times 10^{-2}\,\text{mol/L}.$$

The units come from c° which, again, we didn't write down explicitly.

(b)

$$\begin{aligned}
\Delta_r G_m^\circ &= -RT \ln K_{sp} \\
&= -(8.314\,460\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K}) \ln(1.19 \times 10^{-5}) \\
&= -(8.314\,460\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K})(-11.339) \\
&= 28\,109\,\text{J/mol} \\
&= 28.109\,\text{kJ/mol}.
\end{aligned}$$

Note that we used the rule that the number of significant decimal places in the result of a logarithm is equal to the number of significant digits in the argument.
The standard free energy of reaction can also be expressed in terms of the standard free energies of formation of reactants and products:

$$\begin{aligned}
\Delta_r G_m^\circ &= 2\Delta_f G^\circ(Ag^+) + \Delta_f G^\circ(SO_4^{2-}) - \Delta_f G^\circ(Ag_2SO_4). \\
\therefore \Delta_f G^\circ(Ag_2SO_4) &= 2\Delta_f G^\circ(Ag^+) + \Delta_f G^\circ(SO_4^{2-}) - \Delta_r G_m^\circ \\
&= 2(77.11) + (-744.00) - 28.109\,\text{kJ}\,\text{mol}^{-1} \\
&= -617.89\,\text{kJ}\,\text{mol}^{-1}.
\end{aligned}$$

7. Write a balanced reaction:

$$Fe_{(s)} + 5\,CO_{(g)} \longrightarrow [Fe(CO)_5]_{(s)}$$

$$\begin{aligned}
\Delta_r G_m^\circ &= \Delta_f G^\circ(Fe(CO)_5) - [\Delta_f G^\circ(Fe) + 5\Delta_f G^\circ(CO)] \\
&= -695.0 - [0 + 5(-137.17)]\ \text{kJ}\,\text{mol}^{-1} \\
&= -9.2\,\text{kJ}\,\text{mol}^{-1}.
\end{aligned}$$

We used the fact that the standard free energy of formation of an element (e.g. iron) is, by definition, zero.

$$\begin{aligned}
\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q \\
&= \Delta_r G_m^\circ + RT \ln \left(\frac{1}{(a_{\text{CO}})^5} \right) \\
&= -9.2\,\text{kJ mol}^{-1} + (8.314\,460 \times 10^{-3}\,\text{kJ K}^{-1}\text{mol}^{-1})(298.15\,\text{K}) \ln \left(\frac{1}{(0.23)^5} \right) \\
&= 9.1\,\text{kJ mol}^{-1}.
\end{aligned}$$

Since $\Delta_r G_m > 0$, this reaction will not occur.