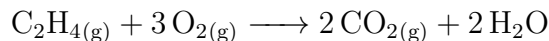


# Chemistry 2000 Fall 2017 Test 2 Version A Solutions

1. Start with a balanced reaction:



(a) **liquid water:**

$$\begin{aligned}\Delta_r S^\circ &= 2S^\circ(\text{CO}_2) + 2S^\circ(\text{H}_2\text{O}, \text{l}) - [S^\circ(\text{C}_2\text{H}_4) + 3S^\circ(\text{O}_2)] \\ &= 2(213.7) + 2(69.940) - [219.22 + 3(205.0)] \text{ J K}^{-1}\text{mol}^{-1} \\ &= -266.9 \text{ J K}^{-1}\text{mol}^{-1}.\end{aligned}$$

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

(b) **water vapor:**

$$\begin{aligned}\Delta_r S^\circ &= 2S^\circ(\text{CO}_2) + 2S^\circ(\text{H}_2\text{O}, \text{g}) - [S^\circ(\text{C}_2\text{H}_4) + 3S^\circ(\text{O}_2)] \\ &= 2(213.7) + 2(188.72) - [219.22 + 3(205.0)] \text{ J K}^{-1}\text{mol}^{-1} \\ &= -29.4 \text{ J K}^{-1}\text{mol}^{-1}.\end{aligned}$$

In (a), the reaction converts 4 gas molecules to 2, 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 positive. Accordingly, there is no temperature at which this reaction would be thermodynamically allowed.
3. (a) See figure 1 for my annotated diagram. There are three triple points (three points where three phases meet).
- (b) The normal freezing point is the freezing point at 1 atm, or 101.325 kPa. This is the point where the solid-liquid coexistence (melting) curve crosses the line  $\log_{10}(p/\text{kPa}) = \log_{10}(101.325) = 2.006$ . This is the horizontal line in figure 1. Note that the solid phase adjacent to the liquid at this pressure is the **monoclinic** phase. To get the melting temperature, we just drop down from this point to the temperature axis, as shown in the figure. When I did this by hand a few times, I got melting temperatures between 393 and 396 K. I was willing to accept values between 390 and 399 K, but **it was important to show me how you got your value** since (for example), the gas-liquid-monoclinic triple point is found at a very similar temperature.

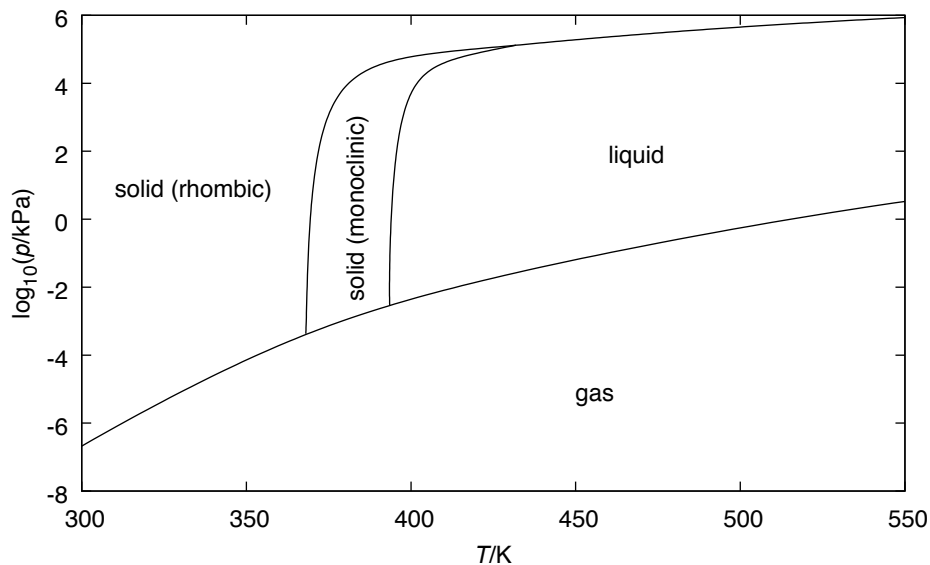


Figure 1: Annotated sulfur phase diagram. The three triple points are circled in red. The horizontal dashed blue lines marks approximately 1 atm. The vertical dashed blue line drops down from where the horizontal line meets the melting curve, thus allowing us to read off the normal melting point from the temperature axis.

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:

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

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

	$T/\text{K}$	$p/\text{bar}$
1:	396.07	$2.388 \times 10^{-4}$
2:	433.69	$2.206 \times 10^{-3}$

Now we just have to substitute everything into the equation:

$$\begin{aligned}\Delta_{\text{vap}}H^\circ &= \frac{(8.314\,460\,\text{J K}^{-1}\text{mol}^{-1}) \ln \left( \frac{2.206 \times 10^{-3}}{2.388 \times 10^{-4}} \right)}{\frac{1}{396.07} - \frac{1}{433.69\,\text{K}}} \\ &= 84\,405\,\text{J mol}^{-1} \\ &\equiv 84.40\,\text{kJ mol}^{-1}.\end{aligned}$$

5. (a) The melting point is  $T = -11.5 + 273.15\,\text{K} = 261.7\,\text{K}$ . Calculating  $\Delta_{\text{fus}}S$  is a straightforward application of  $\Delta S = q_{\text{rev}}/T$ :

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} = \frac{11\,234\,\text{J mol}^{-1}}{261.7\,\text{K}} = 42.94\,\text{J K}^{-1}\text{mol}^{-1}.$$

- (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  $11\,234\,\text{J mol}^{-1}$ , then this heat must come from the surroundings. For the surroundings then, we have  $q_{\text{rev}} = -11\,234\,\text{J mol}^{-1}$ .

$$\begin{aligned}\Delta S_{\text{surr}} &= \frac{q_{\text{rev}}}{T} = \frac{-11\,234\,\text{J mol}^{-1}}{273\,\text{K}} = -41.1\,\text{J K}^{-1}\text{mol}^{-1}. \\ \therefore \Delta S_{\text{universe}} &= \Delta S_{\text{surr}} + \Delta_{\text{fus}}S \\ &= -41.1 + 42.94\,\text{J K}^{-1}\text{mol}^{-1} \\ &= 1.8\,\text{J K}^{-1}\text{mol}^{-1} > 0.\end{aligned}$$

Melting of ethylene glycol in a room at  $0^\circ\text{C}$  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 is a little difficult to justify theoretically. 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  $0^\circ\text{C}$ :

$$\begin{aligned}\Delta_{\text{fus}}G &= \Delta_{\text{fus}}H - T\Delta_{\text{fus}}S \\ &= 11\,234\,\text{J mol}^{-1} - (273.15\,\text{K})(42.94\,\text{J K}^{-1}\text{mol}^{-1}) \\ &= -494\,\text{J mol}^{-1} < 0.\end{aligned}$$

Since  $\Delta_{\text{fus}}G$  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  $\Delta G$ . 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  $\Delta G$ .

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



For this reaction, we have the equilibrium expression

$$K_{\text{sp}} = (a_{\text{Ca}^{2+}})(a_{\text{F}^{-}})^2.$$

If the solubility (the number of moles of calcium fluoride that dissolve per litre of water) is  $s$ , then we have (neglecting  $c^\circ$ , which has the value 1 mol/L)  $a_{\text{Ca}^{2+}} = s$  and  $a_{\text{F}^{-}} = 2s$ . Therefore

$$\begin{aligned} K_{\text{sp}} &= s(2s)^2 = 4s^3. \\ \therefore s^3 &= K_{\text{sp}}/4 = (1.61 \times 10^{-10})/4 = 4.03 \times 10^{-11}. \\ \therefore s &= (4.03 \times 10^{-11})^{1/3} = 3.43 \times 10^{-4} \text{ mol/L}. \end{aligned}$$

The units come from  $c^\circ$  which, again, we didn't write down explicitly.

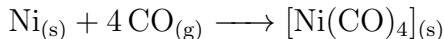
(b)

$$\begin{aligned} \Delta_r G_m^\circ &= -RT \ln K_{\text{sp}} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(1.61 \times 10^{-10}) \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})(-22.550) \\ &= 55 \text{ 900 J/mol} \\ &= 55.900 \text{ kJ/mol}. \end{aligned}$$

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:

$$\begin{aligned} \Delta_r G_m^\circ &= \Delta_f G^\circ(\text{Ca}^{2+}) + 2\Delta_f G^\circ(\text{F}^{-}) - \Delta_f G^\circ(\text{CaF}_2). \\ \therefore \Delta_f G^\circ(\text{Ca}^{2+}) &= \Delta_r G_m^\circ - 2\Delta_f G^\circ(\text{F}^{-}) + \Delta_f G^\circ(\text{CaF}_2) \\ &= 55.900 - 2(-281.52) + (-1173.51) \text{ kJ mol}^{-1} \\ &= -554.57 \text{ kJ mol}^{-1}. \end{aligned}$$

7. Write a balanced reaction:



$$\begin{aligned} \Delta_r G_m^\circ &= \Delta_f G^\circ(\text{Ni}(\text{CO})_4) - [\Delta_f G^\circ(\text{Ni}) + 4\Delta_f G^\circ(\text{CO})] \\ &= -589.16 - [0 + 4(-137.17)] \text{ kJ mol}^{-1} \\ &= -40.48 \text{ kJ mol}^{-1}. \end{aligned}$$

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

$$\begin{aligned}\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q \\ &= \Delta_r G_m^\circ + RT \ln \left( \frac{1}{(a_{\text{CO}})^4} \right) \\ &= -40.48 \text{ kJ mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln \left( \frac{1}{(0.15)^4} \right) \\ &= -21.67 \text{ kJ mol}^{-1}.\end{aligned}$$

Since  $\Delta_r G_m < 0$ , this reaction could occur.