

Chemistry 2740 Spring 2016 Test 2 solutions

1. The calculation we need to do consists of three pieces, one of which (the entropy at 298 K) is given:

$$\begin{aligned}
 S^\circ(\text{g}, 399\text{K}) &= S^\circ(\text{l}, 298\text{K}) + \Delta_{298 \rightarrow 399\text{K}}S + \Delta_{\text{vap}}S. \\
 \Delta_{298 \rightarrow 399\text{K}}S &= C_{p,m} \ln \left(\frac{T_2}{T_1} \right) \\
 &= (254.7 \text{ J K}^{-1}\text{mol}^{-1}) \ln \left(\frac{398.7 \text{ K}}{298.15 \text{ K}} \right) \\
 &= 74.02 \text{ J K}^{-1}\text{mol}^{-1}. \\
 \Delta_{\text{vap}}S &= \frac{\Delta_{\text{vap}}H^\circ}{T} \\
 &= \frac{34.41 \text{ kJ mol}^{-1}}{398.7 \text{ K}} = 86.31 \text{ J K}^{-1}\text{mol}^{-1}. \\
 \therefore S_g &= 361.2 \text{ J K}^{-1}\text{mol}^{-1} + 74.02 \text{ J K}^{-1}\text{mol}^{-1} + 86.31 \text{ J K}^{-1}\text{mol}^{-1} \\
 &= 521.5 \text{ J K}^{-1}\text{mol}^{-1}.
 \end{aligned}$$

2. (a) $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T \Delta_r S_m^\circ$. Since $\Delta_r H_m^\circ < 0$ and $-T \Delta_r S_m^\circ < 0$ for any T , then their sum can only be negative.

(b)

$$\begin{aligned}
 T &= 40 + 273.15 \text{ K} = 313.15 \text{ K}. \\
 \Delta_r G_m^\circ &= \Delta_r H_m^\circ - T \Delta_r S_m^\circ \\
 &= -7.42 \text{ kJ mol}^{-1} - (313.15 \text{ K})(41.56 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1}) \\
 &= -20.43 \text{ kJ mol}^{-1}. \\
 \Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q \\
 &= \Delta_r G_m^\circ + RT \ln \left(\frac{[\text{C}_{70} \cdot \text{L}]}{[\text{C}_{70}][\text{L}]} \right) \\
 &= -20.43 \text{ kJ mol}^{-1} + (8.314472 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(313.15 \text{ K}) \\
 &\quad \times \ln \left(\frac{4.3 \times 10^{-2}}{(1.8 \times 10^{-4})(5.2 \times 10^{-5})} \right) \\
 &= 19.51 \text{ kJ mol}^{-1}.
 \end{aligned}$$

Since $\Delta_r G_m$ is positive, the *reverse* reaction is the one we would expect to occur, i.e. the dissociation of the complex into $\text{C}_{70} + \text{L}$.

Bonus: First, let's think about why a positive $\Delta_r S^\circ$ is surprising here. We're taking two molecules in solution, each of which has a great deal of orientational freedom and, in the case of L, a certain amount of conformational freedom (rotation around

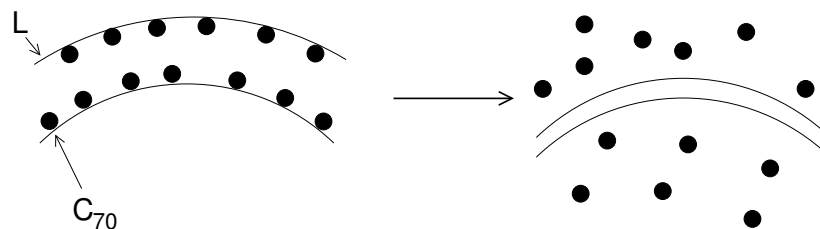


Figure 1: Sketch of the release of solvent during the complexation process. The solvent, chloroform, is represented by the filled circles. C_{70} and L are represented in cross-section. Chloroform is polar, and π systems are very polarizable, so there are relatively strong dipole-induced dipole forces between the reactants and the solvent. In order for C_{70} and L to bind, the solvent held by the faces that will come into contact has to be expelled, leading to a large increase in entropy associated with the increased freedom of these solvent molecules. Note that solvent would stick to both sides of L. The solvent molecules on the outer face are not shown, for simplicity.

single bonds), and we're sticking them together. Because of π - π interactions, we expect L to drape itself over C_{70} . In fact, if you look at it carefully, you will see that some of the parts of L look like the building blocks of C_{70} . There is a large loss of conformational freedom when we do that, so there should be (at first glance) an increase in entropy.

When you run into reactions in solution with unexpected entropy changes, blame the solvent. When individually solvated, each of these molecules is surrounded by loosely bound solvent molecules. The solvent molecules on the sides of these molecules that will come together must be released in order for the two molecules to form the complex. (Figure 1 shows what I mean by this.) Because these are large molecules, there are many solvent molecules associated with each of them, so the release of these bound solvent molecules causes a large increase in entropy. Similar effects are often responsible for an increase in entropy during the binding of a substrate to an enzyme in aqueous solution.

3. (a) $4^3 = 64$
- (b) There are only $64 - 3 = 61$ codons that can be included in the protein-coding sequence. Thus, the number of different protein-coding sequences of 333 codons is 61^{333} .
- (c) $S = k_B \ln \Omega = k_B \ln (61^{333}) = 333k_B \ln 61$.
- (d) $S = k_B \ln (20^{333}) = 333k_B \ln(20)$. This is smaller than the entropy of a random protein-coding DNA sequence. This makes sense because the DNA code is redundant, i.e. more than one codon codes for most amino acids. Thus, the protein sequence requires less information to specify than the DNA sequence does.