7.014 Section Problem: Thermodynamics

Given the reversible chemical reaction: \( A + B \rightleftharpoons C + D \)

and the equation:
\[
\Delta G = \Delta G^0 + RT \ln \frac{[\text{products}]}{[\text{reactants}]}
\]

at 25\(^\circ\)C, \( RT = 0.59 \text{ kcal mol}^{-1} \)
at 37\(^\circ\)C, \( RT = 0.61 \text{ kcal mol}^{-1} \)

a) If \( \Delta G = 0 \), what does this mean?

b) If \( \Delta G^0 = 0 \), what does this mean?

c) In the living cell at 25 \(^\circ\)C, you observe the following concentrations:
\[
[A] = 50 \text{ M} \quad [B] = 30 \text{ M} \quad [C] = 1 \text{ M} \quad [D] = 10 \text{ M}
\]

If you allow a reaction mixture of only A, B, C, and D to come to equilibrium at 25 \(^\circ\)C, you observe these concentrations:
\[
[A] = 100 \text{ M} \quad [B] = 100 \text{ M} \quad [C] = 10 \text{ M} \quad [D] = 10 \text{ M}
\]

i) What is \( \Delta G^0 \) for this reaction?

ii) What is \( \Delta G^0 \) for the reaction \( C + D \rightleftharpoons A + B \)?

iii) What is \( \Delta G \) for this reaction in the living cell?

iv) How can you explain the difference between \( \Delta G \) and \( \Delta G^0 \)?
Solutions to Thermodynamics

The equation:

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]

at 25°C, \( RT = 0.59 \text{ kcal mol}^{-1} \)  

at 37°C, \( RT = 0.61 \text{ kcal mol}^{-1} \)

holds under all conditions

\( \Delta G^0 \) is the free energy of the reaction under standard conditions: all \([\text{]}\)'s = 1M

\( \Delta G \) is the free energy of the reaction under any specified conditions; that is, where you’ve specified the \([\text{]}\)'s of all compounds involved in the reaction.

a) In order to find \( \Delta G \), you must specify a set of conditions. If, under those specified set of conditions, \( \Delta G = 0 \), the reaction is at equilibrium at those conditions and no net formation of products or reactants will occur. If \( \Delta G < 0 \), net formation of products will occur; if \( \Delta G > 0 \), net formation of reactants will occur.

b) If \( \Delta G^0 = 0 \), the reaction is at equilibrium at standard conditions; that is, when all \([\text{]}\)'s = 1M, it will be at equilibrium. This is a possible, but unusual situation.

c) i) In order to calculate \( \Delta G^0 \), you need to know the \([\text{]}\)'s at equilibrium; that is, when \( \Delta G=0 \). In that case, the above equation becomes:

\[ 0 = \Delta G^0 + RT \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \quad \text{or} \quad \Delta G^0 = -RT \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]

in our case: \( \Delta G^0 = -RT \ln \left( \frac{\text{[C][D]}}{\text{[A][B]}} \right) \) at equilibrium.

This relationship only applies at equilibrium (when \( \Delta G=0 \)), so we must use the equilibrium \([\text{]}\)'s:

\[ \Delta G^0 = -RT \ln \left( \frac{10 \times 10^6}{100 \times 10^6} \right) \left( \frac{10 \times 10^6}{100 \times 10^6} \right) = -0.59 \text{ kcal mol}^{-1} \ln \left( \frac{10^{10}}{10^{18}} \right) = +2.72 \text{ kcal mol}^{-1} \]

This means that if all \([\text{]}\)'s = 1M, the reaction would spontaneously proceed to the left.

ii) For the reverse reaction \( (\text{C} + \text{D} \rightleftharpoons \text{A} + \text{B}) \), the sign of \( \Delta G^0 \) is reversed (-2.72).
iii) In the living cell, which is virtually never at equilibrium, you must use the complete $\Delta G$ equation:

$$
\Delta G = \Delta G^0 + RT \ln \left( \frac{[products]}{[reactants]} \right)
$$

Substituting in our values gives:

$$
\Delta G = +2.72 \text{ kcal/mol} + 0.59 \frac{\text{kcal}}{\text{mol}} \ln \frac{\left(1 \times 10^6\right)\left(10 \times 10^6\right)}{\left(50 \times 10^6\right)\left(30 \times 10^6\right)} = +2.72 \frac{\text{kcal}}{\text{mol}} - 2.95 \frac{\text{kcal}}{\text{mol}} = 0.24 \frac{\text{kcal}}{\text{mol}}
$$

This means that, in the living cell, the reaction proceeds spontaneously to the right. Often, living cells are able to drive unfavorable reactions by removing the products as soon as they are formed (thus lowering $[products]$ and thereby lowering $\Delta G$) or synthesizing the reactants very rapidly (thus increasing $[reactants]$ and thereby lowering $\Delta G$).