CHEM 361A - Lecture 8 Activity
Free Energies

In Class

1. When solutions containing DNA strands with complementary sequences are mixed, the strands react to form double helices. This process is illustrated in Figure 1

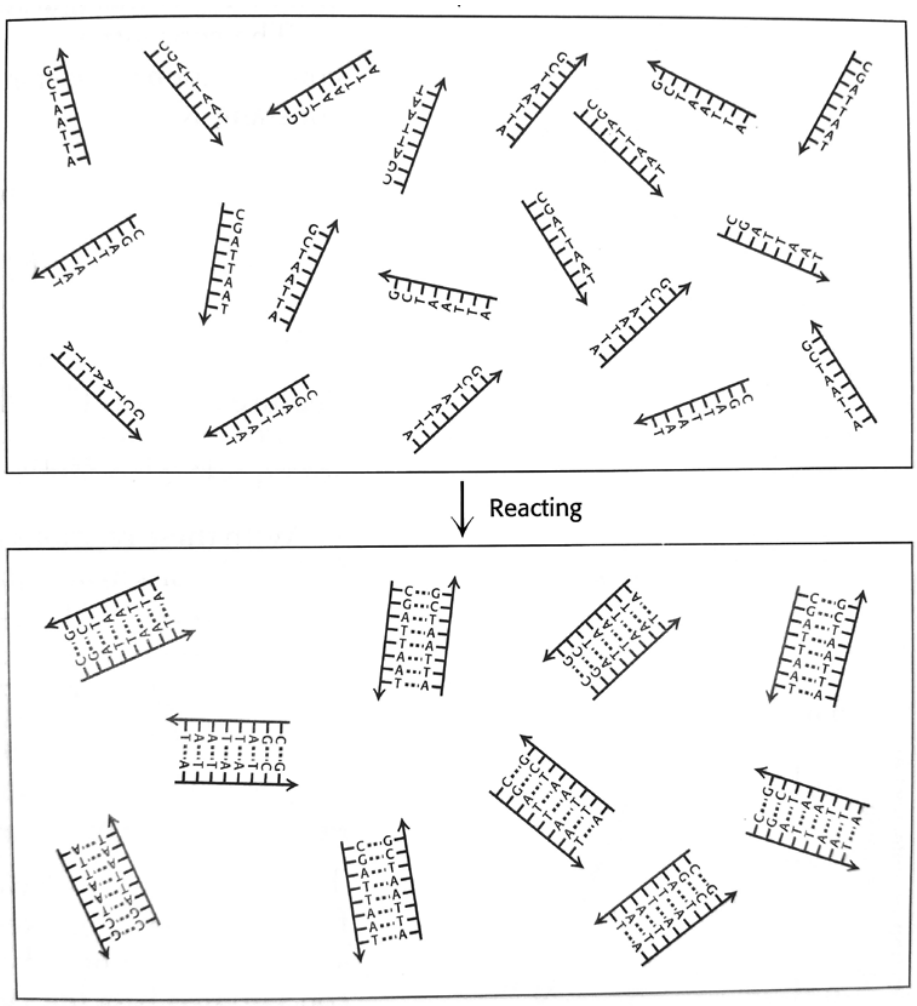

Figure 1: Scheme of DNA mixing process.

(a) Through the reaction process illustrated in Figure 1, did the entropy go up or down?

(b) If the reaction process is spontaneous, what must the sign for ΔH be?

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta H - T\Delta S < 0$ $\quad T > 320$

2. As an approximation, we can assume that proteins exist either in native (or physiologically functioning) state and the denatured state. For a certain protein $\Delta H^{\ominus} = 512$ kJ mol^{-1} and $\Delta S^{\ominus} = 1.60$ kJ K^{-1} mol^{-1} for the native to denatured process. At what temperature does denaturation becomes spontaneous?

3. The standard state in biochemistry is slightly different than in Physical Chemistry. In biochemistry the hydrogen-ion concentration for the standard state is 10^{-7} M, because the physiological pH is about 7. Because of this change in the standard state of the concentration of H^+, we will employ a slightly different notation for the standard change in Gibbs Free Energy ($\Delta G^{\ominus\prime}$).

   Many chemical and biological reactions are not spontaneous ($\Delta G > 0$). However, in certain cases, these reactions become spontaneous when they are coupled with a spontaneous process.

   (a) For example consider the following reaction:

   $$\begin{aligned} A &\rightleftharpoons B + C & \Delta G^{\ominus\prime} &= 21 \text{ kJ mol}^{-1} \\ B &\rightleftharpoons D & \Delta G^{\ominus\prime} &= -34 \text{ kJ mol}^{-1} \end{aligned}$$

   i. Is the process $A \rightleftharpoons B + C$ spontaneous?

   ii. Determine the $\Delta G^{\ominus\prime}$ for the process $A \rightleftharpoons C + D$. Is this process spontaneous?

   (b) The conversion of glucose to glucose-6-phosphate in glycosis is catalysed by a family of enzymes called hexokinases. The $\Delta_r G^{\ominus\prime}$ for this reaction is

   $$\text{glucose} + P_i \rightleftharpoons \text{glucose}-6\text{-phosphate} + H_2O;\ \Delta_r G^{\ominus\prime} = 13.8 \text{ kJ mol}^{-1}$$

   i. Is this process spontaneous?

   ii. In order for this process to be spontaneous, ATP must be consumed

   $$ATP + H_2O \rightleftharpoons ADP + P_i;\ \Delta_r G^{\ominus\prime} = \text{-}30.3 \text{ kJ mol}^{-1}$$

   Write the balanced chemical equation for the conversion of glucose to glucose-6-phosphate coupled with the conversion of ATP to ADP and determine the $\Delta_r G^{\ominus\prime}$ for the coupled reaction. Is this process now spontaneous?

4. Benzene is an important organic chemical compound given that it is an elementary petrochemical used to synthesize more complex structures.

   (a) Given that the normal (i.e. p = 1 atm) boiling temperature of benzene is 355.9 K and the vapour pressure of liquid benzene is 1.10×10^4 Pa at 20.0°C, show that its $\Delta_{vap}H = 30.7$ kJ mol^{-1}

   (b) A triple point of a given compound can be found when the vapour pressure of the solid state and the liquid state are equal. Given that $\Delta_{fus}H = 9.95$ kJ mol^{-1} and the vapour pressure of solid benzene is 137 Pa at −44.3°C, determine the triple point temperature and pressure of benzene.

Homework

5. A quantity of 0.35 moles of an ideal gas initially at 288.8 K is expanded from 1.2 L to 7.4 L. Calculate the values of w, q, ΔU, ΔS and ΔG if the process is carried out

   (a) Isothermally and reversibly ($w = -1530$ J; $q = 1530$ J; $\Delta U = 0$ J; $\Delta S = 5.3$ J K^{-1}; $\Delta G = -1530$ J)

   (b) Isothermally and irreversibly against an external pressure of 1.0 atm ($w = -630$ J; $q = 630$ J; $\Delta U = 0$ J; $\Delta S = 5.3$ J K^{-1}; $\Delta G = -1530$ J)

6. Determine the values for $\Delta_r G^{\ominus}$ for the following alcohol fermentation reaction ($\Delta_r G^{\ominus} = -222.7$ kJ mol^{-1}):

$$\alpha\text{-D}-\text{glucose(aq)} \longrightarrow 2\,\text{C}_2\text{H}_5\text{OH(l)} + 2\,\text{CO}_2\text{(g)}$$

   Thermodynamic data:

   - α-D$-$glucose(aq): $\Delta_f G^{\ominus} = -914.5$ kJ mol^{-1}
   - C_2H_5OH(l): $\Delta_f G^{\ominus} = -174.2$ kJ mol^{-1}
   - CO_2(g): $\Delta_f G^{\ominus} = -394.4$ kJ mol^{-1}

7. From the following reactions at 298 K:

$$\text{fumarate}^{2-} + \text{NH}_4{}^{+} \rightleftharpoons \text{asparatate}^{-};\ \Delta_r G^{\ominus\prime} = -36.7 \text{ kJ mol}^{-1}$$
$$\text{fumarate}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{malate}^{2-};\ \Delta_r G^{\ominus\prime} = -2.9 \text{ kJ mol}^{-1}$$

   For the following reaction

$$\text{malate}^{2-} + \text{NH}_4{}^{+} \rightleftharpoons \text{aspartate}^{-} + \text{H}_2\text{O}$$

   (a) Calculate $\Delta_r G^{\ominus\prime}$ for the malate to aspartate process. (-33.8 kJ mol^{-1})

   (b) Is the malate to fumarate process spontaneous? ($\Delta G > 0$: No)

   (c) Is the malate to asparatate process spontaneous? ($\Delta G < 0$: Yes)

8. You are trying to better define the solid-liquid phase boundary of a new substance by performing a couple of measurements. This new substance has a molar mass of 147.2 g mol^{-1}. At its normal (i.e. p = 1 atm) melting temperature of 372 K, the densities of its solid and liquid phase are 987 and 923 kg m^{-3}, respectively. If the pressure is increased to 1.0×10^7 Pa, the melting temperature increases to 385 K. Calculate Δ_{fus}H for this substance. ($\Delta_{fus} H = 2.97 \times 10^3$ J mol^{-1})

9. Butane is an important fuel used in many application including lighter fuel for camping stoves. Its enthalpy of vaporization is 22.4 kJ mol^{-1} and its normal boiling temperature (1 atm) is 272.7 K. Its enthalpy of fusion is 4.66 kJ mol^{-1} and the vapour pressure of the solid is 0.21 Pa at 120 K.

   (a) Determine the temperature that butane will boil at the summit of Mt Everest if the pressure is 32 kPa. (244.2 K)

   (b) A triple point of a given compound can be found when the vapour pressure of the solid state and the liquid state are equal. Determine the triple point temperature and pressure of butane. (134.9 K; 4.2 Pa)