

Chapter 03

1. a.

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

$$\Delta G^\circ = \left(-280 \frac{\text{kJ}}{\text{mol}}\right) - (298 \text{ K}) \left(-0.790 \frac{\text{kJ}}{\text{mol} \times \text{K}}\right) = -44.6 \frac{\text{kJ}}{\text{mol}}$$

b. $\Delta G^\circ = 0$ @ T_m . Unfolding will be favorable at temperatures above the T_m .

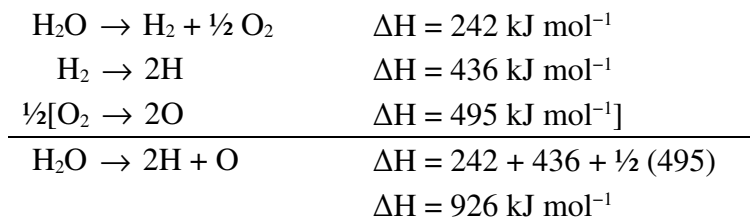
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 0 = \left(-280 \frac{\text{kJ}}{\text{mol}}\right) - (x \text{ K}) \left(-0.790 \frac{\text{kJ}}{\text{mol} \times \text{K}}\right)$$

$$-354.4 \text{ K} = -x$$

$$x = 354.4 \text{ K or } 81.3 \text{ }^\circ\text{C}.$$

2. a. Reversing the direction of the reaction as written requires a reversal of the sign on ΔH . Also, when summing two or more reactions, the species that appear on both sides cancel; thus:



b. The reaction has two O-H bonds broken; therefore, the energy of a single O-H bond is $926/2 = 463 \text{ kJ mol}^{-1}$.

3. a. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$

$$= [(109.6 \text{ kJ mol}^{-1}) - (-30.5 \text{ kJ mol}^{-1})]/298 \text{ K}$$

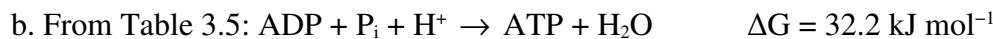
$$= 470 \text{ J K}^{-1} \text{ mol}^{-1}$$

b. The decomposition products are both gasses, and therefore have significantly more translational and rotational freedom compared to the initial solid. Thus, entropy increases.

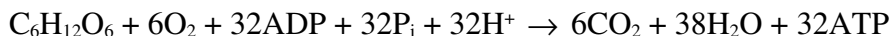
4. a. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= (-2816 \text{ kJ mol}^{-1}) - (310 \text{ K})(0.181 \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= -2872.1 \text{ kJ mol}^{-1}$$



$$(32.2 \text{ kJ mol}^{-1}) \times (32 \text{ ATP}) = 1030.4 \text{ kJ mol}^{-1}$$



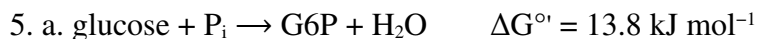
$$\Delta G = (-2872.1 \text{ kJ mol}^{-1}) + (1030.4 \text{ kJ mol}^{-1})$$

$$= -1841.7 \text{ kJ mol}^{-1}$$

c. %efficiency = $|\Delta G^\circ_{\text{ATP synthesis}} / \Delta G^\circ_{\text{total available}}| \times 100\%$

$$= (1030.4/2872.1) \times 100$$

$$= 35.9\%$$



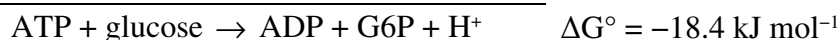
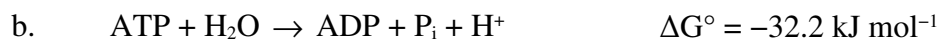
$$K_{\text{eq}} = ([\text{G6P}][\text{H}_2\text{O}]/[\text{glucose}] \times [\text{P}_i]) = e^{-\Delta G^\circ/RT}$$

Note: In the biochemical standard state, the activity of H_2O is assigned a value of 1.

$$([\text{G6P}](1))/((0.005) \times (0.005)) = e^{(-13.8)/(0.008314) \times (310)}$$

$$[\text{G6P}] = 0.000025 \times e^{-5.36}$$

$$[\text{G6P}] = 1.2 \times 10^{-7} \text{ M}$$



c. $K_{\text{eq}} = ([\text{G6P}] \times [\text{ADP}] \times [\text{H}^+])/([\text{ATP}] \times [\text{glucose}]) = e^{-\Delta G^\circ/RT}$

Note: The activity of H^+ is referenced to a biochemical standard state concentration of $1 \times 10^{-7} \text{ M}$.

$$K_{\text{eq}} = ([\text{G6P}] \times 0.001 \times 10^{-0.4})/(0.003 \times 0.005) = e^{-(-18.4)/(0.008314) \times (310)}$$

$$[\text{G6P}] = (0.000015 \times e^{7.14})/(0.001 \times 10^{-0.4}) = (0.0189)/(0.000398)$$

$$= 47.5 \text{ M}$$

This G6P concentration is never reached because G6P is continuously consumed by other reactions, and so the reaction never reaches true thermodynamic equilibrium.

6. a. $K_{\text{eq}} = ([\text{GAP}]/[\text{DHAP}]) = e^{-\Delta G^\circ/RT}$

$$K_{\text{eq}} = ([\text{GAP}]/[\text{DHAP}]) = e^{-7.5/(0.008314) \times (310)}$$

$$K_{\text{eq}} = [\text{GAP}]/[\text{DHAP}] = 5.4 \times 10^{-2}$$

$$\begin{aligned}
 \text{b. } \Delta G &= \Delta G^\circ + RT \ln([GAP]/[DHAP]) \\
 &= (7.5 \text{ kJ mol}^{-1}) + (0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})(310 \text{ K}) \ln(0.01) \\
 &= -4.37 \text{ kJ mol}^{-1}
 \end{aligned}$$

7. a. ΔS must be positive because the increase in isoenergetic conformations in the denatured state increases the entropy of the denatured state relative to the folded state.

b. Since $\Delta G = \Delta H - T\Delta S$, a positive value for ΔS results in a negative contribution to ΔG (T is always positive in the Kelvin scale). Thus, for proteins to be stably folded (which requires ΔG to be positive for the process described in the question), it would appear that ΔH must be large and positive. This is generally true; however, this simple analysis does not consider the hydrophobic effect, which results in a more negative overall ΔS (see Problems 8 and 9, and further elaboration of this topic in Chapter 6). Thus, the requirement that ΔH is large and positive is not absolute because the hydrophobic effect reduces the magnitude of ΔS .

8. This process reduces the entropy of the solvent water, which becomes more ordered in the clathrate structures. This is the hydrophobic effect.

9. a. We expect ΔS for denaturation to be positive due to the increase in conformational entropy. If ΔH is also positive (energy is required to break the noncovalent interactions in the folded state), the +,+ situation described in Table 3.3 pertains. Under these conditions, the denaturation process goes from being unfavorable at lower temperature to being favorable at higher temperature.

b. In cases of cold denaturation, the sign on ΔS is dominated by the hydrophobic effect and is therefore negative. In these cases, ΔH must also be negative (see Table 3.3) for the process to become favorable as temperature decreases. Clathrate cage formation would account for the sign of ΔH being negative (favorable) for cold denaturation.

10. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -RT \ln K$, thus

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

Divide both sides by $-RT$.

$$-(\Delta H^\circ/RT) + \Delta S^\circ/R = \ln K$$

This is the van't Hoff equation.

$$\ln K = (-\Delta H^\circ/R) \times (1/T) + \Delta S^\circ/R$$

If ΔH° and ΔS° are independent of temperature, a graph of $\ln K$ versus $1/T$ should be a straight line with slope $-\Delta H^\circ/R$. These values can also be determined from direct fits to the K versus T data using nonlinear curve-fitting software.

11. a. See Problem 10. Plot $\ln K_w$ versus $1/T$ and fit a line to the points. The slope will correspond to $-\Delta H^\circ/R$.

$1/T$	$\ln K_w$
0.00366	-34.4
0.00336	-32.2
0.00330	-31.9
0.00323	-31.3

$$\ln K_w = (-7093.9 \text{ K})(1/T) - 8.426$$

$$\text{slope} = -7093.9 \text{ K} = -\Delta H^\circ/R$$

$$-7093.9 \text{ K} = -\Delta H^\circ/(0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$\Delta H^\circ = 59.0 \text{ kJ mol}^{-1}$$

$$\text{b. } \ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$$

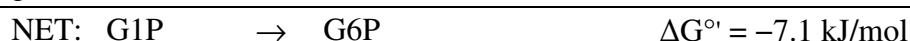
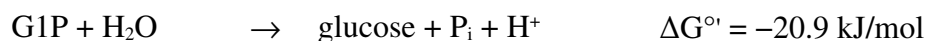
$$\Delta S^\circ = [\ln K + (\Delta H^\circ/RT)] \times R = [R \ln K + (\Delta H^\circ/T)]$$

$$\Delta S^\circ = ((0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (\ln(10^{-14})) + (59.0 \text{ kJ mol}^{-1}/(\times 298 \text{ K})))$$

$$\Delta S^\circ = (-0.268 \text{ kJ mol}^{-1} \text{ K}^{-1}) + (0.198 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$\Delta S^\circ = -0.070 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ or } -70 \text{ J mol}^{-1} \text{ K}^{-1}$$

12. a.



$$K = e^{-\left(\frac{\Delta G^{\circ'}}{RT}\right)} = e^{-\left(\frac{-7.1}{0.008314 \times 298}\right)}$$

$$K = 17.6$$

b. The favored direction for the reaction can be determined by comparing K to Q . From part (a) we know that $K = 17.6$. $Q = 1/(0.001) = 1000$. Thus, $Q > K$, and therefore the reverse reaction is favored. This conclusion is also borne out by the (much more time-consuming) calculation of ΔG :

$$\Delta G = \Delta G^{\circ'} + RT \ln \left(\frac{[\text{G6P}]}{[\text{G1P}]} \right) = -7.1 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol} \times \text{K}} \right) (298 \text{ K}) \ln \left(\frac{1}{0.001} \right) = +5.93 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G = -7.1 \frac{\text{kJ}}{\text{mol}} + 17.1 \frac{\text{kJ}}{\text{mol}} = +10.0 \frac{\text{kJ}}{\text{mol}}$$

Since $\Delta G > 0$ the reverse reaction, formation of G1P, is favored.

13. To be favorable, the reaction must have $\Delta G < 0$.

$$0 > \Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{oxaloacetate}][\text{NADH}][\text{H}^+]}{[\text{malate}][\text{NAD}^+]} \right)$$

$$0 > +29.7 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol} \times \text{K}} \right) (310\text{K}) \ln \left(\frac{[\text{oxaloacetate}][0.0003][1]}{[0.0004][0.020]} \right)$$

$$-11.5 > \ln \left(\frac{[\text{oxaloacetate}][0.0003][1]}{[0.0004][0.020]} \right) = \ln(37.5[\text{oxaloacetate}])$$

$$e^{-11.5} = 9.89 \times 10^{-6} > 37.5[\text{oxaloacetate}]$$

$$2.63 \times 10^{-7} > [\text{oxaloacetate}]$$

Thus, the reaction is unfavorable under these conditions when [oxaloacetate] exceeds 2.63×10^{-7} M.

14. $350 \text{ kJ/hour} \times 24 \text{ hours/day} = 8400 \text{ kJ/day}$

Palmitate combustion = $-9977.6 \text{ kJ mol}^{-1}$

$8400 \text{ kJ}/(9977.6 \text{ kJ mol}^{-1}) = 0.842 \text{ mols palmitate}$

Palmitate formula: $\text{C}_{16}\text{H}_{32}\text{O}_2$

Molar mass = $16(12.011) + 32(1.0079) + 2(16) = 256.4 \text{ g/mol}$

$256.4 \text{ g/mol} \times 0.842 \text{ mols} = 216 \text{ g palmitate}$

15. a. For a mole of protein molecule, $\Delta S = R \ln W - R \ln 1$, where W is the number of conformations available to each and R is the gas constant, $8.314 \text{ J/K} \cdot \text{mol}$. Because there are 99 bonds between 100 residues, $W = 3^{99}$.

a. $\Delta S = 9.04 \times 10^2 \text{ J/K} \cdot \text{mol}$.

15. b. folded \leftrightarrow unfolded

@ $\frac{1}{2}$ denaturation, [folded] = [unfolded]

Therefore, $K_{\text{eq}} = 1$. This defines the “melting” temperature of the protein.

Since,

$$\begin{aligned} \Delta H^\circ - T\Delta S^\circ &= -RT \ln K_{\text{eq}} \\ &= 0 \end{aligned}$$

Then,

$$\begin{aligned}\Delta H^\circ &= T\Delta S^\circ \\ &= (323 \text{ K}) \times 904 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 292.2 \text{ kJ mol}^{-1}\end{aligned}$$

15. c. Since both ΔH° and ΔS° are positive, the fraction denatured will increase with increasing temperature.

16. a.

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{glucose}_{in}]}{[\text{glucose}_{out}]} \right) = 0 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol} \times \text{K}} \right) (310 \text{ K}) \ln \left(\frac{0.0001}{0.00001} \right) = +5.93 \frac{\text{kJ}}{\text{mol}}$$

For transport of 10^{-6} mol glucose:

$$\Delta G = \left(+5.93 \frac{\text{kJ}}{\text{mol}} \right) \times (10^{-6} \text{ mol}) = +5.93 \times 10^{-6} \text{ kJ}$$

b.

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{glucose}_{in}]}{[\text{glucose}_{out}]} \right) = 0 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol} \times \text{K}} \right) (310 \text{ K}) \ln \left(\frac{0.001}{0.010} \right) = -5.93 \frac{\text{kJ}}{\text{mol}}$$

For transport of 10^{-6} mol glucose:

$$\Delta G = \left(-5.93 \frac{\text{kJ}}{\text{mol}} \right) \times (10^{-6} \text{ mol}) = -5.93 \times 10^{-6} \text{ kJ}$$

c.

$$\frac{\text{energy required for transport}}{\text{energy available from ATP hydrolysis}} = \frac{5.93 \times 10^{-6} \text{ kJ}}{30.5 \frac{\text{kJ}}{\text{mol ATP}}} = 1.94 \times 10^{-7} \text{ mol ATP}$$

Thus, $> 1.94 \times 10^{-7}$ mol ATP are required to drive the reaction in part (a) forward (i.e., to make $\Delta G < 0$). No ATP hydrolysis is required for the reaction in part (b) as ΔG is already < 0 .

17. a.

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{ethanol}][\text{NAD}^+][\text{CO}_2]}{[\text{pyruvate}][\text{NADH}][\text{H}^+]^2} \right)$$

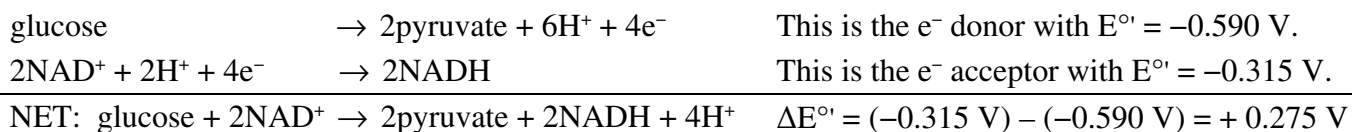
$$\begin{aligned}
 -38.3 \frac{\text{kJ}}{\text{mol}} &= -64.4 \frac{\text{kJ}}{\text{mol}} + RT \ln \left(\frac{(\text{ethanol}) \left(\frac{0.000350 \text{ M}}{1 \text{ M}} \right) \left(\frac{15 \text{ torr}}{750 \text{ torr}} \right)}{\left(\frac{62 \times 10^{-6} \text{ M}}{1 \text{ M}} \right) \left(\frac{15 \times 10^{-6} \text{ M}}{1 \text{ M}} \right) \left(\frac{10^{-7.4} \text{ M}}{10^{-7.0} \text{ M}} \right)^2} \right) \\
 -38.3 \frac{\text{kJ}}{\text{mol}} &= -64.4 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol}} \right) (310 \text{ K}) \ln \left(\frac{(\text{ethanol}) \times (7.0 \times 10^{-6})}{1.47 \times 10^{-10}} \right) \\
 +26.1 \frac{\text{kJ}}{\text{mol}} &= 2.577 \frac{\text{kJ}}{\text{mol}} \ln \left[(\text{ethanol}) \times (4.75 \times 10^4) \right] \\
 e^{\left(\frac{26.1 \frac{\text{kJ}}{\text{mol}}}{2.577 \frac{\text{kJ}}{\text{mol}}} \right)} &= \left[(\text{ethanol}) \times (4.75 \times 10^4) \right] = 2.50 \times 10^4 \\
 (\text{ethanol}) &= \frac{2.50 \times 10^4}{4.75 \times 10^4} = 0.527
 \end{aligned}$$

Thus, [ethanol] = 0.527 M.

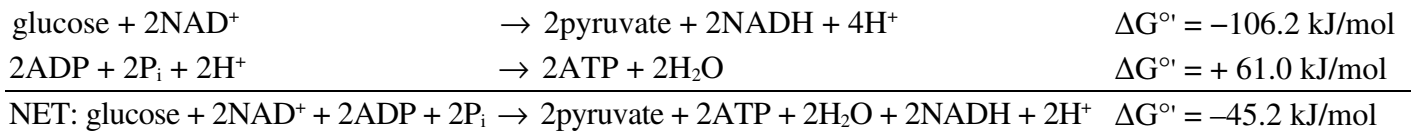
b.

$$\Delta G = \Delta G^{\circ'} + RT \ln \left(\frac{[\text{pyruvate}]^2 [\text{ATP}]^2 [\text{H}_2\text{O}]^2 [\text{NADH}]^2 [\text{H}^+]^2}{[\text{glucose}] [\text{ADP}]^2 [\text{P}_i]^2 [\text{NAD}^+]^2} \right)$$

Evaluation of $\Delta G^{\circ'}$ requires combination of $\Delta G^{\circ'}$ values for ATP hydrolysis (given) and glucose oxidation (which can be calculated from the $E^{\circ'}$ info provided):



Thus, $\Delta G^{\circ'} = -nF\Delta E^{\circ'} = -(4)(96.5 \text{ kJ/mol} \times \text{V})(+0.275 \text{ V}) = -106.2 \text{ kJ/mol}$.



$$\Delta G = -45.2 \frac{\text{kJ}}{\text{mol}} + RT \ln \left(\frac{(62 \times 10^{-6})^2 (0.0031)^2 (1)^2 (15 \times 10^{-6})^2 (10^{-0.4})^2}{(0.0051)(2.2 \times 10^{-4})^2 (0.0059)^2 (3.5 \times 10^{-4})^2} \right)$$

$$\Delta G = -45.2 \frac{\text{kJ}}{\text{mol}} + \left(0.008314 \frac{\text{kJ}}{\text{mol}} \right) (310\text{K}) \ln(1.25 \times 10^{-3}) = -62.4 \frac{\text{kJ}}{\text{mol}}$$