

1. Consider a reaction $R \rightleftharpoons P$ in which $\Delta H = -20. \text{ kJ/mol}$ and $\Delta S = 10. \text{ J/mol} \cdot \text{K}$.

- Calculate the ΔG for this reaction at 25°C .
- Is the reaction spontaneous (explain your answer)?

a.

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

$$\Delta G = -20,000 \text{ J/mol} - 298.15 \text{ K} \times 10 \text{ J/mol}\cdot\text{K} = -22,981.5 \text{ J/mol} \approx -23 \text{ kJ/mol}$$

b.

Since we have a negative ΔG , this reaction is spontaneous.

2. Consider the isomerization reaction $R \rightleftharpoons P$, in which R is converted to P. The ΔG° for this reaction is $-10. \text{ kJ/mol}$. Calculate the $[P]/[R]$ at equilibrium at 25°C .

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$K_{\text{eq}} = [P]/[R] = e^{-(\Delta G^\circ/RT)} = e^{-(10,000 \text{ J/mol} / 8.314 \text{ J/mol}\cdot\text{K} \times 298.15 \text{ K})} = 56.5$$

At equilibrium the ratio of $[P] : [R]$ is $56.5 : 1$

3. Phosphoglucosmutase catalyses the reaction in which a phosphate group is transferred from the Carbon 1 of glucose to the Carbon 6 of glucose ($G1P \rightleftharpoons G6P$). A student at OU incubates a 0.2 M solution of glucose-1-phosphate overnight with a small amount of the enzyme. At equilibrium the concentration of glucose 1-phosphate is $9.0 \times 10^{-3} \text{ M}$ and the concentration of glucose 6-phosphate is $19.1 \times 10^{-2} \text{ M}$.

Calculate the equilibrium constant (K_{eq}) and the standard state free energy (ΔG°) for this reaction at 25°C .

$$K_{\text{eq}} = [G6P]/[G1P] = 19.1 \times 10^{-2} \text{ M} / 9 \times 10^{-3} \text{ M} = 21.2$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$\Delta G^\circ = - 8.314 \text{ J/mol}\cdot\text{K} \times 298.15 \text{ K} \times \ln 21.2 \approx -7.57 \text{ kJ/mol}$$

4. Consider the following reactions at 25°C for which $\Delta G^\circ = 0$, and $[A] = [B] = [C] = 1 \text{ mM}$



What is ΔG for each of the above cases?

$$1) \Delta G = \Delta G^{\circ} + RT \ln Q = 0 + 8.314 \text{ J/K}\cdot\text{mol} \times 298.15 \text{ K} \times \ln (0.001\text{M} \times 0.001\text{M} / 0.001\text{M})$$

$$\Delta G \approx -17.1 \text{ kJ/mol}$$

$$2) \Delta G = \Delta G^{\circ} + RT \ln Q = 0 + 8.314 \text{ J/K}\cdot\text{mol} \times 298.15 \text{ K} \times \ln (0.001\text{M} / 0.001\text{M} \times 0.001\text{M})$$

$$\Delta G \approx 17.1 \text{ kJ/mol}$$

$$3) \Delta G = \Delta G^{\circ} + RT \ln Q = 0 + 8.314 \text{ J/K}\cdot\text{mol} \times 298.15 \text{ K} \times \ln (0.001\text{M} / 0.001\text{M})$$

$$\Delta G = 0$$

5. F₀F₁ ATPase is a fully reversible motor enzyme that can transport protons against pH gradient when supplied with ATP. Assuming that transport of one proton is coupled to hydrolysis of one ATP, what is the lowest pH that F₀F₁ ATPase can generate outside of the mitochondrial membrane in the absence of other proton-generating fluxes (e.g. complete inhibition of electron transport chain, other transporters, etc)? Assume that pH inside mitochondria is 7.0, [ATP] = 1 mM, [ADP] = 0.1 mM, [HPO₄] = 1 mM.

First, it is important to see the transport as two separate processes coupled together. The first process is the hydrolysis of ATP:



The second process is the flux of protons from inside the mitochondria to its outer membrane:



We can calculate the free energy for the ATP hydrolysis by using the following equation:

$$\Delta G_{\text{ATP}} = \Delta G^{\circ} + RT \ln Q \quad (\Delta G^{\circ} \text{ for ATP hydrolysis is } -30.5 \text{ kJ/mol})$$

$$\Delta G_{\text{ATP}} = -30,500 \text{ J/mol} + 8.314 \text{ J/K}\cdot\text{mol} \times 298.5 \text{ K} \ln (0.0001\text{M} \times 0.001\text{M} / 0.001\text{M})$$

$$\Delta G_{\text{ATP}} \approx -53.33 \text{ kJ/mol}$$

We can solve ΔG for the proton flux in the following manner:

$$\Delta G_{\text{H}^+} = \Delta G^{\circ} + RT \ln Q = 0 \text{ J/mol} + RT \ln ([\text{H}^+]_{\text{outside}} / [\text{H}^+]_{\text{inside}})$$

$$\Delta G_{\text{H}^+} = RT (\log ([\text{H}^+]_{\text{outside}} / [\text{H}^+]_{\text{inside}})) / \log e = 5.7 \text{ kJ/mol} (\log [\text{H}^+]_{\text{outside}} - \log [\text{H}^+]_{\text{inside}})$$

$$\Delta G_{\text{H}^+} = 5.7 \text{ kJ/mol} \times \Delta \text{pH}$$

Now we can set them equal to calculate the pH:

$$\Delta G_{\text{H}^+} = \Delta G_{\text{ATP}}$$

$$5.7 \text{ kJ/mol} \times \Delta \text{pH} = -53.33 \text{ kJ/mol}$$

$$\Delta \text{pH} = -53.33 \text{ kJ/mol} / 5.7 \text{ kJ/mol} = -9.4$$

$$\text{Final pH} = -9.4 + 7 = -2.4$$