Key for Thermodynamics of Metabolism

Metabolism is the set of reactions that in cells that sustains life. A collection of reactions that accomplish a particular need is called a metabolic pathways. One important metabolic pathway is glycolysis in which the combustion of glucose, $C_6H_{12}O_6$, produces water and carbon dioxide:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Characterize this reaction's thermodynamic favorability with respect to temperature. The standard state free energy of formation, standard state enthalpy of formation, and the absolute entropy for glucose are shown here; you will find other necessary thermodynamic values on handouts from earlier in the semester:

$\Delta G_f^o = -910.52$ kJ/mol$_{\text{rxn}}$	$\Delta H_f^o = -1274.4$ kJ/mol$_{\text{rxn}}$	$S^o = 212.1$ J/K $\bullet$ mol$_{\text{rxn}}$

Answer: The values of ΔH^o and ΔS^o are –2806 kJ/mol$_{\text{rxn}}$ and 255.9 J/K $\bullet$ mole$_{\text{rxn}}$), respectively. Given the signs for ΔH^o and ΔS^o, the reaction is favorable at all temperatures.

Suppose a person who weighs 60 kg eats a candy bar that contains 60 g of glucose. Assuming that a person's body is a perfect calorimeter (not a good assumption, of course!) and that the specific heat of a person's body is the same as that for water (not a great assumption, but not unreasonable either), calculate the change in body temperature resulting from the combustion of glucose?

Answer: The heat released by the combustion of glucose, q_{rxn}, is

$$q_{rxn} = \frac{-2806 \text{ kJ}}{\text{mol}_{\text{rxn}}} \times \frac{1\text{mol}_{\text{rxn}}}{\text{mol } C_6H_{12}O_6} \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6} \times 60 \text{ g } C_6H_{12}O_6 = -934.3 \text{ kJ}$$

We know that $q_{body} = -q_{rxn}$, so the body is absorbing 934.3 kJ of heat, thus

$$q_{body} = 934.3 \text{ kJ} = mS\Delta T = (60,000 \text{ g}) \times (4.184 \times 10^{-3} \text{ kJ/g} \bullet \text{C°}) \times \Delta T$$

or a ΔT of 3.7°C.

In your experience as a consumer of candy bars, is this answer reasonable? Explain. If the answer isn't reasonable, then provide at least one plausible explanation—other than a person's body is not a perfect calorimeter—to explain why the calculated ΔT is larger or smaller than expected.

Answer: Of course this answer is unreasonable as we know that eating a candy bar does not cause us to become feverish. The reason the body's temperature does not increase is that the reaction does not release this energy in a single, concentrated burst. Instead, the overall reaction is the result of a multistep process in which the energy is released bit-by-bit. And, of course, much of this energy is used to accomplish useful chemical work, including driving reactions that are thermodynamically unfavorable on their own.

Here is some information about the glycolytic pathway. The first step in the pathway is the transfer of a phosphate from adenosine-triphosphate (ATP) to glucose:

Reaction 1: glucose + ATP $\rightarrow$ glucose-6-phosphate + ADP

Under standard state conditions and in the absence of ATP, glucose-6-phosphate is unstable and reacts with water to produce glucose and a free phosphate:

Reaction 2: glucose-6-phosphate + H_2O $\rightarrow$ glucose + phosphate

Finally, for the hydrolysis of ATP under standard state conditions

Reaction 3: ATP + H_2O $\rightarrow$ ADP + phosphate

the free energy change is $\Delta G^o = -32.48$ kJ/mol$_{\text{rxn}}$.

Given this information, predict the sign of ΔG^o for Reaction 2 under standard state conditions? Explain your reasoning.

Answer: We know that glucose-6-phosphate "is unstable and reacts with water to produce glucose and a free phosphate," which means that the reaction is favorable and that $\Delta G < 0$.

Given the information above, under standard state conditions, the sign of ΔG^o for Reaction 1 is unclear. Using Hess's law, what can you say about the value of ΔG^o for this reaction? State your answer as ΔG^o is greater than..., or ΔG^o is less than..., or ΔG^o is equal to... *Hint: Note that Reaction 3 is the sum of Reactions 1 and 2.*

Answer: From the hint, we know that

$$\Delta G^o_{Rxn3} = \Delta G^o_{Rxn1} + \Delta G^o_{Rxn2}$$

$$-32.48 \text{ kJ/mol}_{\text{rxn}} = \Delta G^o_{Rxn1} + \Delta G^o_{Rxn2}$$

$$\Delta G^o_{Rxn1} = -32.48 \text{ kJ/mol}_{\text{rxn}} + \Delta G^o_{Rxn2}$$

From this we can deduce that $\Delta G^o_{Rxn1} > -32.48$ kJ/mol$_{\text{rxn}}$ because we know that the value of ΔG^o_{Rxn2} is negative. As long as ΔG^o_{Rxn2} is less negative than ΔG^o_{Rxn1}, the pathway is favorable even if ΔG^o_{Rxn1} is positive.

Another step in the glycolytic pathway is

fructose-1,6-diphosphate $\rightarrow$ dihydroxyacetone phosphate + glyceraldehyde-3-phosphate

for which ΔG^o is +23.8 kJ/mol$_{\text{rxn}}$ at 298 K. Although this reaction is unfavorable under standard state conditions, we know it routinely occur in cells; thus, the concentrations of reactants and products in the cells must not be at their standard states values. What is the largest reaction quotient, Q, that will produce a favorable free energy change? Recall that Q is a measure of the relative amounts of products to reactants.

Answer: If the reaction occurs, then ΔG is less than zero. To find the largest Q for a favorable reaction, we recall that $\Delta G = \Delta G^o + RT\ln Q$ and find the value of Q that yields $\Delta G = 0$; thus

$$0 = +23.8 \text{ kJ/mol}_{rxn} + 8.314 \times 10^{-3} \text{ J/K} \bullet \text{mol}_{\text{rxn}} \times 298 \text{ K} \times \ln Q$$

for which a Q that is less than 6.35×10^{-5} yields a favorable reaction.

The value of Q is approximately 10^{-4} in the cells of rats. What is the value of ΔG for this reaction under these conditions and what does this tell you about the favorability of this glycolytic pathway in rats? If you believe that the reaction is unfavorable, why might it still occur?

Answer: Given a Q of 10^{-4} and our prediction that it must be less than 6.35×10^{-5} for a favorable reaction, we expect that the reaction is not favorable; however, a rat's body temperature is not 25°C, but is closer to 38°C, or 311 K; thus

$$\Delta G = +23.8 \text{ kJ/mol}_{\text{rxn}} + 8.314 \times 10^{-3} \text{ J/K} \bullet \text{mol}_{\text{rxn}} \times 311 \text{ K} \times \ln(10^{-4}) = -0.015 \text{ kJ/mol}_{\text{rxn}}$$