Chapter 13 Principles of Bioenergetics

Multiple Choice Questions

1. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 1 Ans: E
If the $\Delta G'^{\circ}$ of the reaction A $\rightarrow$ B is –40 kJ/mol, under standard conditions the reaction:

A) is at equilibrium.
B) will never reach equilibrium.
C) will not occur spontaneously.
D) will proceed at a rapid rate.
E) will proceed spontaneously from left to right.

2. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 1 Ans: C
For the reaction A $\rightarrow$ B, $\Delta G'^{\circ}$ = –60 kJ/mol. The reaction is started with 10 mmol of A; no B is initially present. After 24 hours, analysis reveals the presence of 2 mmol of B, 8 mmol of A. Which is the most likely explanation?

A) A and B have reached equilibrium concentrations.
B) An enzyme has shifted the equilibrium toward A.
C) B formation is kinetically slow; equilibrium has not been reached by 24 hours.
D) Formation of B is thermodynamically unfavorable.
E) The result described is impossible, given the fact that $\Delta G'^{\circ}$ is –60 kJ/mol.

3. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 2 Ans: A
When a mixture of 3-phosphoglycerate and 2-phosphoglycerate is incubated at 25 °C with phosphoglycerate mutase until equilibrium is reached, the final mixture contains six times as much 2-phosphoglycerate as 3-phosphoglycerate. Which one of the following statements is most nearly correct, when applied to the reaction as written? (R = 8.315 J/mol·K; T = 298 K)

3-Phosphoglycerate $\rightarrow$ 2-phosphoglycerate

A) $\Delta G'^{\circ}$ is –4.44 kJ/mol.
B) $\Delta G'^{\circ}$ is zero.
C) $\Delta G'^{\circ}$ is +12.7 kJ/mol.
D) $\Delta G'^{\circ}$ is incalculably large and positive.
E) $\Delta G'^{\circ}$ cannot be calculated from the information given.

4. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 2 Ans: D
When a mixture of glucose 6-phosphate and fructose 6-phosphate is incubated with the enzyme phosphohexose isomerase (which catalyzes the interconversion of these two compounds) until equilibrium is reached, the final mixture contains twice as much glucose 6-phosphate as fructose 6-phosphate. Which one of the following statements is best applied to this reaction outlined below?
(R = 8.315 J/mol·K; T = 298 K)
Glucose 6-phosphate $\rightarrow$ fructose 6-phosphate

A) $\Delta G'^{\circ}$ is incalculably large and negative.
B) $\Delta G'^{\circ}$ is –1.72 kJ/mol.
C) $\Delta G'^{\circ}$ is zero.
D) $\Delta G'^{\circ}$ is +1.72 kJ/mol.
E) $\Delta G'^{\circ}$ is incalculably large and positive.

5. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 1 Ans: A
Hydrolysis of 1 M glucose 6-phosphate catalyzed by glucose 6-phosphatase is 99% complete at equilibrium (i.e., only 1% of the substrate remains). Which of the following statements is most nearly correct? (R = 8.315 J/mol·K; T = 298 K)

A) $\Delta G'^{\circ}$ = –11 kJ/mol
B) $\Delta G'^{\circ}$ = –5 kJ/mol
C) $\Delta G'^{\circ}$ = 0 kJ/mol
D) $\Delta G'^{\circ}$ = +11 kJ/mol
E) $\Delta G'^{\circ}$ cannot be determined from the information given.

6. **Bioenergetics and thermodynamics**
Page: 492 Difficulty: 2 Ans: C
The reaction A + B $\rightarrow$ C has a $\Delta G'^{\circ}$ of –20 kJ/mol at 25° C. Starting under standard conditions, one can predict that:

A) at equilibrium, the concentration of B will exceed the concentration of A.
B) at equilibrium, the concentration of C will be less than the concentration of A.
C) at equilibrium, the concentration of C will be much greater than the concentration of A or B.
D) C will rapidly break down to A + B.
E) when A and B are mixed, the reaction will proceed rapidly toward formation of C.

7. **Bioenergetics and thermodynamics**
Page: 493 Difficulty: 1 Ans: A
Which of the following compounds has the largest negative value for the standard free-energy change ($\Delta G'^{\circ}$) upon hydrolysis?

A) Acetic anhydride
B) Glucose 6-phosphate
C) Glutamine
D) Glycerol 3-phosphate
E) Lactose

8. Bioenergetics and thermodynamics
Page: 494 Difficulty: 1 Ans: E
For the following reaction, $\Delta G'^{\circ} = +29.7$ kJ/mol.
L-Malate + $NAD^+ \rightarrow$ oxaloacetate + NADH + H^+
The reaction as written:

A) can never occur in a cell.
B) can occur in a cell only if it is coupled to another reaction for which $\Delta G'^{\circ}$ is positive.
C) can occur only in a cell in which NADH is converted to NAD^+ by electron transport.
D) cannot occur because of its large activation energy.
E) may occur in cells at some concentrations of substrate and product.

9. Bioenergetics and thermodynamics
Page: 494 Difficulty: 1 Ans: A
For the reaction $A \rightarrow B$, the K_{eq}' is 10^4. If a reaction mixture originally contains 1 mmol of A and no B, which one of the following must be true?

A) At equilibrium, there will be far more B than A.
B) The rate of the reaction is very slow.
C) The reaction requires coupling to an exergonic reaction in order to proceed.
D) The reaction will proceed toward B at a very high rate.
E) $\Delta G'^{\circ}$ for the reaction will be large and positive.

10. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2 Ans: A
In glycolysis, fructose 1,6-bisphosphate is converted to two products with a standard free-energy change ($\Delta G'^{\circ}$) of 23.8 kJ/mol. Under what conditions encountered in a normal cell will the free-energy change (ΔG) be negative, enabling the reaction to proceed spontaneously to the right?

A) Under standard conditions, enough energy is released to drive the reaction to the right.
B) The reaction will not go to the right spontaneously under any conditions because the $\Delta G'^{\circ}$ is positive.
C) The reaction will proceed spontaneously to the right if there is a high concentration of products relative to the concentration of fructose 1,6-bisphosphate.
D) The reaction will proceed spontaneously to the right if there is a high concentration of fructose 1,6-bisphosphate relative to the concentration of products.
E) None of the above conditions is sufficient.

11. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2 Ans: C
During glycolysis, glucose 1-phosphate is converted to fructose 6-phosphate in two successive reactions:
Glucose 1-phosphate $\rightarrow$ glucose 6-phosphate $\Delta G'^{\circ} = -7.1$ kJ/mol
Glucose 6-phosphate $\rightarrow$ fructose 6-phosphate $\Delta G'^{\circ} = +1.7$ kJ/mol
$\Delta G'^{\circ}$ for the overall reaction is:

A) –8.8 kJ/mol.
B) –7.1 kJ/mol.
C) –5.4 kJ/mol.
D) +5.4 kJ/mol.
E) +8.8 kJ/mol.

12. Bioenergetics and thermodynamics
Pages: 494-495 Difficulty: 2 Ans: B
The standard free-energy changes for the reactions below are given.

Phosphocreatine → creatine + P_i $\Delta G'^\circ = -43.0$ kJ/mol

ATP → ADP + P_i $\Delta G'^\circ = -30.5$ kJ/mol

What is the overall $\Delta G'^\circ$ for the following reaction?
Phosphocreatine + ADP → creatine + ATP

A) –73.5 kJ/mol
B) –12.5 kJ/mol
C) +12.5 kJ/mol
D) +73.5 kJ/mol
E) $\Delta G'^\circ$ cannot be calculated without K_{eq}'.

13. Bioenergetics and thermodynamics
Pages: 494-495 Difficulty: 3 Ans: C
The $\Delta G'^\circ$ values for the two reactions shown below are given.

$$\text{Oxaloacetate} + \text{acetyl-CoA} + H_2O \xrightarrow[\text{citrate synthase}]{} \text{citrate} + \text{CoASH} \qquad \Delta G'^\circ = -32.2 \text{ kJ/mol}$$

$$\text{Oxaloacetate} + \text{acetate} \xrightarrow[\text{citrate lyase}]{} \text{citrate} \qquad \Delta G'^\circ = -1.9 \text{ kJ/mol}$$

What is the $\Delta G'^\circ$ for the hydrolysis of acetyl-CoA?
$\text{Acetyl-CoA} + H_2O \longrightarrow \text{acetate} + \text{CoASH} + H^+$

A) –34.1 kJ/mol
B) –32.2 kJ/mol
C) –30.3 kJ/mol
D) +61.9 kJ/mol
E) +34.1 kJ/mol

14. Phosphoryl group transfers and ATP
Page: 496-500 Difficulty: 2 Ans: B
All of the following contribute to the large, negative, free-energy change upon hydrolysis of “high-energy” compounds *except:*

A) electrostatic repulsion in the reactant.
B) low activation energy of forward reaction.
C) stabilization of products by extra resonance forms.
D) stabilization of products by ionization.
E) stabilization of products by solvation.

15. **Phosphoryl group transfers and ATP**
Page: 496 Difficulty: 1 Ans: E
The hydrolysis of ATP has a large negative $\Delta G'^{\circ}$; nevertheless it is stable in solution due to:

A) entropy stabilization.
B) ionization of the phosphates.
C) resonance stabilization.
D) the hydrolysis reaction being endergonic.
E) the hydrolysis reaction having a large activation energy.

16. **Phosphoryl group transfers and ATP**
Page: 497 Difficulty: 3 Ans: E
The hydrolysis of phosphoenolpyruvate proceeds with a $\Delta G'^{\circ}$ of about –62 kJ/mol. The greatest contributing factors to this reaction are the destabilization of the reactants by electostatic repulsion and stabilization of the product pyruvate by:

A) electrostatic attraction.
B) ionization.
C) polarization.
D) resonance.
E) tautomerization.

17. **Phosphoryl group transfers and ATP**
Page: 499 Difficulty: 1 Ans: B
Which one of the following compounds does *not* have a large negative free energy of hydrolysis?

A) 1,3-bis phosphoglycerate
B) 3-phosphoglycerate
C) ADP
D) Phosphoenolpyruvate
E) Thioesters (e.g. acetyl-CoA)

18. **Phosphoryl group transfers and ATP**
Page: 504 Difficulty: 1 Ans: B
The immediate precursors of DNA and RNA synthesis in the cell all contain:

A) 3' triphosphates.
B) 5' triphosphates.
C) adenine.
D) deoxyribose.
E) ribose.

19. **Phosphoryl group transfers and ATP**
Page: 504 Difficulty: 2 Ans: A
Muscle contraction involves the conversion of:

A) chemical energy to kinetic energy.
B) chemical energy to potential energy.
C) kinetic energy to chemical energy.
D) potential energy to chemical energy.
E) potential energy to kinetic energy.

20. Biological oxidation-reduction reactions
Page: 507 Difficulty: 1 Ans: D
Biological oxidation-reduction reactions *always* involve:

A) direct participation of oxygen.
B) formation of water.
C) mitochondria.
D) transfer of electron(s).
E) transfer of hydrogens.

21. Biological oxidation-reduction reactions
Pages: 508-510 Difficulty: 2 Ans: B
The standard reduction potentials ($E'°$) for the following half reactions are given.

Fumarate + $2H^+ + 2e^- \rightarrow$ succinate	$E'° = +0.031$ V
FAD + $2H^+ + 2e^- \rightarrow FADH_2$	$E'° = –0.219$ V

If you mixed succinate, fumarate, FAD, and $FADH_2$ together, all at l M concentrations and in the presence of succinate dehydrogenase, which of the following would happen *initially*?

A) Fumarate and succinate would become oxidized; FAD and $FADH_2$ would become reduced.
B) Fumarate would become reduced, $FADH_2$ would become oxidized.
C) No reaction would occur because all reactants and products are already at their standard concentrations.
D) Succinate would become oxidized, FAD would become reduced.
E) Succinate would become oxidized, $FADH_2$ would be unchanged because it is a cofactor.

22. Biological oxidation-reduction reactions
Pages: 508-510 Difficulty: 3 Ans: E
$E'°$ of the NAD^+/NADH half reaction is –0.32 V. The $E'°$ of the oxaloacetate/malate half reaction is –0.175 V. When the concentrations of NAD^+, NADH, oxaloacetate, and malate are all 10^{-5} M, the "spontaneous" reaction is:

A) Malate + $NAD^+ \rightarrow$ oxaloacetate + NADH + H^+.
B) Malate + NADH + $H^+ \rightarrow$ oxaloacetate + NAD^+.
C) NAD^+ + NADH + $H^+ \rightarrow$ malate + oxaloacetate.
D) NAD^+ + oxaloacetate $\rightarrow$ NADH + H^+ + malate.
E) Oxaloacetate + NADH + $H^+ \rightarrow$ malate + NAD^+.

23. Biological oxidation-reduction reactions
Page: 513 Difficulty: 2 Ans: A
The structure of NAD^+ does *not* include:

A) a flavin nucleotide.
B) a pyrophosphate bond.
C) an adenine nucleotide.
D) nicotinamide.
E) two ribose residues.

Short Answer Questions

24. Bioenergetics and thermodynamics
Pages: 490-491 Difficulty: 2
Explain the relationships among the change in the degree of order, the change in entropy, and the change in free energy that occur during a chemical reaction.

Ans: Entropy is a measure of disorder. Thus, if there is an increase in order there is a decrease in entropy. The greater the entropy of a system, the smaller its free energy. Thus, an increase in entropy during a reaction will result in a decrease in free energy.

25. Bioenergetics and thermodynamics
Pages: 491-492 Difficulty: 2
Consider the reaction: A + B $\rightarrow$ C + D. If the equilibrium constant for this reaction is a large number (say, 10,000), what do we know about the standard free-energy change ($\Delta G'^{\circ}$) for the reaction? Describe the relationship between K_{eq}' and $\Delta G'^{\circ}$.

Ans: $\Delta G'^{\circ} = -RT \ln K_{eq}'$. If K_{eq}' is a large (positive) number, the term $-RT \ln K_{eq}'$ (and therefore $\Delta G'^{\circ}$) has a relatively large, negative value.

26. Bioenergetics and thermodynamics
Page: 492 Difficulty: 2
The standard free energy change ($\Delta G'^{\circ}$) for ATP hydrolysis is –30.5 kJ/mol. ATP, ADP, and P_i are mixed together at initial concentrations of 1 M of each, then left alone until the reaction: ADP + P_i $\rightarrow$ ATP has come to equilibrium. For each species (i.e., ATP, ADP, and P_i) indicate whether the concentration will be equal to 1 M, less than 1 M, or greater than 1 M.

Ans: At equilibrium, ATP < 1 M; ADP > 1 M; P_i > 1 M.

27. Bioenergetics and thermodynamics
Page: 492 Difficulty: 3
If a 0.1 M solution of glucose 1-phosphate is incubated with a catalytic amount of phosphoglucomutase, the glucose 1-phosphate is transformed to glucose 6-phosphate until equilibrium is reached. At equilibrium, the concentration of glucose 1-phosphate is 4.5×10^{-3} M and that of glucose 6-phosphate is 8.6×10^{-2} M. Set up the expressions for the calculation of K_{eq}' and $\Delta G'^{\circ}$ for this reaction (in the direction of glucose 6-phosphate formation). (R = 8.315 J/mol·K; T = 298 K)

Ans: $K_{eq}' = \dfrac{[\text{glucose 6-phosphate}]}{[\text{glucose 1-phosphate}]} = \dfrac{0.086\text{ M}}{0.0045\text{ M}} = 19$

$$\Delta G'^{\circ} = -RT \ln K_{eq}' = -(8.315\text{ J/mol·K})(298\text{ K})(\ln 19) = -7.3\text{ kJ/mol}$$

28. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2
What is the difference between ΔG and $\Delta G'^{\circ}$ of a chemical reaction? Describe, quantitatively, the relationship between them.

Ans: $\Delta G'^{\circ}$ is the difference in free energies of the products and reactants at standard conditions. Thus, it is a physical constant, characteristic of each chemical reaction. ΔG is a variable that depends on $\Delta G'^{\circ}$, the temperature, and the concentrations of all reactants and products:

$$\Delta G = \Delta G'^{\circ} + RT \ln \frac{[\text{product}]}{[\text{reactant}]}$$

29. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2
The following expression for the actual free-energy change for the reaction
A + B $\rightarrow$ C + D is incorrect.
$\Delta G = \Delta G'^{\circ} + RT \ln K_{eq}'$
Why is it wrong, and what is the correct expression for the real free-energy change of this reaction?

Ans: The correct expression is: $$\Delta G = \Delta G'^{\circ} + RT \ln \frac{[C][D]}{[A][B]}$$
Substitution of K_{eq}' for the concentration term is valid only for the special case in which these concentrations represent the *equilibrium* concentrations. In this situation, $\Delta G = 0$.

30. Bioenergetics and thermodynamics
Page: 494 Difficulty: 3
Explain in quantitative terms the circumstances under which the following reaction can proceed.
Citrate $\rightarrow$ isocitrate $\Delta G'^{\circ} = +13.3$ kJ/mol

Ans: A reaction for which $\Delta G'^{\circ}$ is positive can proceed under conditions in which ΔG is negative. From the relationship
$$\Delta G = \Delta G'^{\circ} + RT \ln \frac{[\text{product}]}{[\text{reactant}]}$$
it is clear that if the concentration of product is kept very low (by its subsequent metabolic removal, for instance), the logarithmic term becomes negative and ΔG can then have a negative value.

31. Bioenergetics and thermodynamics
Pages: 491-404 Difficulty: 2
Explain why each of the following statements is false.
(a) In a reaction under standard conditions, only the reactants are fixed at 1 M.
(b) When $\Delta G'^{\circ}$ is positive, $K_{eq}' > 1$.
(c) ΔG and $\Delta G'^{\circ}$ mean the same thing.
(d) When $\Delta G'^{\circ} = 1.0$ kJ/mol, $K_{eq}' = 1$.

Ans: (a) Both reactants and products are fixed at 1 M. (b) $\Delta G'^{\circ} = -RT \ln K_{eq}'$, so when $\Delta G'^{\circ} < 0$, the term $-RT \ln K_{eq}'$ has a negative value and $K_{eq}' > 1$. (c) $\Delta G'^{\circ}$ is the difference in free energies of the products and reactants at standard conditions, and is a constant, characteristic of each chemical reaction. ΔG is a variable that depends on $\Delta G'^{\circ}$, the temperature, and the concentrations of all reactants and products

$$\Delta G = \Delta G'^{\circ} + RT \ln \frac{[\text{product}]}{[\text{reactant}]}$$
(d) $\Delta G'^{\circ} = -RT \ln K_{eq}'$. When $\Delta G'^{\circ} = 1$, $K_{eq}' < 1$.

32. Bioenergetics and thermodynamics
Page: 494 Difficulty: 3
In glycolysis, the enzyme pyruvate kinase catalyzes this reaction:
Phosphoenolpyruvate + ADP $\rightarrow$ pyruvate + ATP

Given the information below, show how you would calculate the equilibrium constant for this reaction. (R = 8.315 J/mol·K; T = 298 K)

Reaction 1) ATP $\rightarrow$ ADP + P_i $\Delta G'^\circ$ = –30.5 kJ/mol
Reaction 2) phosphoenolpyruvate $\rightarrow$ pyruvate + P_i $\Delta G'^\circ$ = –61.9 kJ/mol

Ans: The reaction is the sum of reaction 2 and the reverse of reaction 1. Therefore, $\Delta G'^\circ$ = –31.4 kJ/mol.

$$\Delta G'^\circ = -RT \ln K_{eq}'$$
$$\ln K_{eq}' = -\Delta G'^\circ/RT$$
$$= 31.4 \text{ kJ/mol} / [(8.315 \text{ J/mol·K})(298 \text{ K})]$$
$$\ln K_{eq}' = 12.672$$
$$K_{eq}' = 3.19 \times 10^5$$

33. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2
Explain what is meant by the statement: "Standard free-energy changes are additive." Give an example of the usefulness of this additive property in understanding how cells carry out thermodynamically unfavorable chemical reactions.

Ans: When two chemical reactions can be summed to give a third reaction, the standard free-energy change for the third reaction is the arithmetic sum of the standard free-energy changes of the other two reactions. Many possible examples may be given. (See p. 498 for one such example.)

34. Bioenergetics and thermodynamics
Page: 494 Difficulty: 2
Given $\Delta G'^\circ$ for each of the following reactions,
1. ATP $\rightarrow$ ADP + P_i $\Delta G'^\circ$ = –30.5 kJ/mol
2. glucose 6-phosphate $\rightarrow$ glucose + P_i $\Delta G'^\circ$ = –13.8 kJ/mol

show how you would calculate the standard free-energy change ($\Delta G'^\circ$) for the reaction:
3. ATP + glucose $\rightarrow$ glucose 6-phosphate + ADP

Ans: Reaction 3 is the sum of reaction 1 and the reversal of reaction 2. Because of the additivity of free energy changes, the overall $\Delta G'^\circ$ for reaction 3 is the sum of the free energy changes for reaction 1 and the reversal of reaction 2:
1. ATP $\rightarrow$ ADP + P_i $\Delta G_1'^\circ$ = –30.5 kJ/mol
2. glucose + P_i $\rightarrow$ glucose 6-phosphate $\Delta G_2'^\circ$ = +13.8 kJ/mol
3. ATP + glucose $\rightarrow$ ADP + glucose 6-phosphate

$\Delta G_3'^\circ = \Delta G_1'^\circ + \Delta G_2'^\circ$ = (–30.5 + 13.8) kJ/mol = –16.7 kJ/mol

35. Phosphoryl group transfers and ATP
Pages: 496-497 Difficulty: 2
Why is the actual free energy (ΔG) of hydrolysis of ATP in the cell different from the standard free energy ($\Delta G'^\circ$)?

Ans: The concentrations of the reactant (ATP) and the products (ADP and P_i) are not all equal to 1 M. The pH is not exactly equal to 7.0 (the standard pH) and the temperature is usually higher than the standard temperature of 25 °C.

36. Phosphoryl group transfers and ATP
Page: 497 Difficulty: 2
The free energy of hydrolysis of phosphoenolpyruvate is –61.9 kJ/mol. Rationalize this large, negative value for $\Delta G'^{\circ}$ in chemical terms.

Ans: The product of hydrolysis is enol pyruvate, which quickly tautomerizes to pyruvate. This keto-enol tautomerization stabilizes the products of hydrolysis relative to phosphoenolpyruvate, which cannot tautomerize.

37. Phosphoryl group transfers and ATP
Page: 500 Difficulty: 3
In general, when ATP hydrolysis is coupled to an energy-requiring reaction, the actual reaction often consists of the transfer of a phosphate group from ATP to another substrate, rather than an actual hydrolysis of the ATP. Explain.

Ans: Hydrolysis of the ATP would result in the loss of most of the free energy as heat. In a transfer reaction, the gamma (third) phosphate of ATP is transferred to the reaction substrate to produce a high-energy phosphorylated intermediate, which can then form the product in an exergonic reaction.

38. Phosphoryl group transfers and ATP
Pages: 504-505 Difficulty: 2
The first law of thermodynamics states that the amount of energy in the universe is constant, but that the various forms of energy can be interconverted. Describe four different types of such energy transduction that occur in living organisms and provide one example for each.

Ans: Conversion of:
- chemical to osmotic energy (ATP-driven active transport across a membrane)
- electromagnetic to electrical energy (light-induced electron flow in chloroplasts)
- chemical to electromagnetic energy (ATP-dependent photon emission in fireflies)
- chemical to mechanical energy (ATP-driven muscle contraction)

Other answers are possible.

39. Biological oxidation-reduction reactions
Page: 508 Difficulty: 1
What is an oxidation? What is a reduction? Can an oxidation occur without a simultaneous reduction? Why or why not?

Ans: Oxidation is the loss of electrons; reduction is the gain of electrons. Free electrons are unstable (do not occur), so whenever an electron is released by oxidation of some species, an electron must be accepted by reduction of another species.

40. Biological oxidation-reduction reactions
Page: 510 Difficulty: 3
During transfer of two electrons through the mitochondrial respiratory chain, the overall reaction is:

$$NADH + 1/2\ O_2 + H^+ \rightarrow NAD^+ + H_2O$$

For this reaction, the difference in reduction potentials for the two half-reactions ($\Delta E'^{\circ}$) is +1.14 V. Show how you would calculate the standard free-energy change, $\Delta G'^{\circ}$, for the reaction. (The Faraday constant, $\mathfrak{F}$, is 96.48 kJ/V·mol.)

Ans: $\Delta G'^{\circ} = -n\ \mathfrak{F}\ \Delta E'^{\circ}$
For reactions involving NADH, two electrons are transferred (n = 2). So $\Delta G'^{\circ}$ = (–2)(96.48 kJ/V·mol)(1.14 V) = –220 kJ/mol.

41. Biological oxidation-reduction reactions
Page: 510 Difficulty: 2
If $\Delta E'^{\circ}$ for an oxidation-reduction reaction is positive, will $\Delta G'^{\circ}$ be positive or negative? What is the equation that relates $\Delta G'^{\circ}$ and $\Delta E'^{\circ}$?

Ans: Negative. $\Delta G'^{\circ} = -n\ \mathfrak{F}\ \Delta E'^{\circ}$.

42. Biological oxidation-reduction reactions
Pages: 510-511 Difficulty: 2
Glycerol 3-phosphate dehydrogenase catalyzes the following reversible reaction:

Glycerol 3-phosphate + $NAD^+ \rightarrow$ NADH + H^+ + dihydroxyacetone phosphate

Given the standard reduction potentials below, calculate $\Delta G'^{\circ}$ for the glycerol 3-phosphate dehydrogenase reaction, proceeding from left to right as shown. Show your work. (The Faraday constant, $\mathfrak{F}$, is 96.48 kJ/V·mol.)

Dihydroxyacetone phosphate + $2e^-$ + $2H^+ \rightarrow$ glycerol 3-phosphate $\quad E'^{\circ} = -0.29$ V
$NAD^+ + H^+ + 2e^- \rightarrow$ NADH $\quad E'^{\circ} = -0.32$ V

Ans:

$\Delta E'^{\circ}$ = E'° (electron acceptor) – E'° (electron donor)
= – 0.32 – (–0.29) = –0.03 V
$\Delta G'^{\circ}$ = $-n\ \mathfrak{F}\Delta E'^{\circ}$ = (–2)(96.48 kJ/V·mol)(–0.03 V)
$\Delta G'^{\circ}$ = +5.8 kJ/mol

43. Biological oxidation-reduction reactions
Page: 511 Difficulty: 1
For each pair of ions or compounds below, indicate which is the more highly reduced species.

(a) Co^{2+}/Co^+
(b) Glucose/CO_2
(c) Fe^{3+}/Fe^{2+}
(d) Acetate/CO_2
(e) Ethanol/acetic acid
(f) Acetic acid/acetaldehyde

Ans: (a) Co^+; (b) glucose; (c) Fe^{2+}; (d) acetate; (e) ethanol; (f) acetaldehyde.

44. Biological oxidation-reduction reactions
Page: 511 Difficulty: 3
Lactate dehydrogenase catalyzes the reversible reaction:

$$\text{Pyruvate} + \text{NADH} + H^+ \rightarrow \text{Lactate} + \text{NAD}^+$$

Given the following facts (a) tell in which direction the reaction will tend to go if NAD^+, NADH, pyruvate, and lactate were mixed, all at 1 M concentrations, in the presence of lactate dehydrogenase at pH 7; (b) calculate $\Delta G'^\circ$ for this reaction. Show your work.

$NAD^+ + H^+ + 2e^- \rightarrow NADH$ $E'^\circ = -0.32$ V
pyruvate $+ 2H^+ + 2e^- \rightarrow$ lactate $E'^\circ = -0.19$ V
The Faraday constant, $\mathfrak{F}$, is 96.48 kJ/V·mol.

Ans: $\Delta G'^\circ = E'^\circ(\text{acceptor}) - E'^\circ(\text{donor}) = -0.19 \text{ V} - (-0.32 \text{ V}) = +0.13 \text{ V}$
$\Delta G'^\circ = -n\ \mathfrak{F}\ \Delta E'^\circ = (-2)(96.48 \text{ kJ/V·mol})(0.13 \text{ V})$
$\Delta G'^\circ = -25.1$ kJ/mol

45. Biological oxidation-reduction reactions
Page: 511 Difficulty: 3
Alcohol dehydrogenase catalyzes the following reversible reaction:

$$\text{Acetaldehyde} + \text{NADH} + H^+ \rightarrow \text{Ethanol} + \text{NAD}^+$$

Use the following information to answer the questions below:
Acetaldehyde $+ 2H^+ + 2e^- \rightarrow$ ethanol $E'^\circ = -0.20$ V
$NAD^+ + H^+ + 2e^- \rightarrow NADH$ $E'^\circ = -0.32$ V
The Faraday constant, $\mathfrak{F}$, is 96.48 kJ/V·mol.
(a) Calculate $\Delta G'^\circ$ for the reaction as written. Show your work.
(b) Given your answer to (a), what is the $\Delta G'^\circ$ for the reaction occurring in the reverse direction?
(c) Which reaction (forward or reverse) will tend to occur spontaneously under standard conditions?
(d) In the cell, the reaction actually proceeds in the direction that has a positive $\Delta G'^\circ$. Explain how this could be possible.

Ans:
(a) $\Delta G'^\circ = E'^\circ(\text{acceptor}) - E'^\circ(\text{donor}) = -0.20 - (-0.32) = +0.12\text{V}$
$\Delta G'^\circ = -n\mathfrak{F}\Delta E'^\circ = (-2)(96.48\text{kJ/V·mol})(0.12 \text{ V}) = -23.2$ kJ/mol
(b) For the reverse reaction, $\Delta G'^\circ = +23.2$ kJ/mol.
(c) The forward reaction will occur spontaneously.
(d) A reaction for which $\Delta G'^\circ$ is positive can occur if ΔG is negative.
From the relationship

$$\Delta G = \Delta G'^\circ + RT \ln \frac{[\text{product}]}{[\text{reactant}]}$$

it is clear that if the concentration of product is kept very low (by its removal in a subsequent metabolic step), the log term becomes negative and ΔG can have a negative value.