

MCB 102 Discussion
Bioenergetics Worksheet: Answers
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1. 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? ($R = 8.315 \text{ J/mol}\cdot\text{K}$; $T = 298 \text{ K}$) (A)

3-Phosphoglycerate \rightleftharpoons 2-phosphoglycerate

- A) DG° is -4.44 kJ/mol .
- B) DG° is zero.
- C) DG° is $+12.7 \text{ kJ/mol}$.
- D) DG° is incalculably large and positive.
- E) DG° cannot be calculated from the information given.

2. The reaction $A + B \rightleftharpoons C$ has a DG° 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.

3. During glycolysis, glucose 1-phosphate is converted to fructose 6-phosphate in two successive reactions: ©

Glucose 1-phosphate \rightleftharpoons glucose 6-phosphate $DG^\circ = -7.1 \text{ kJ/mol}$
Glucose 6-phosphate \rightleftharpoons fructose 6-phosphate $DG^\circ = +1.7 \text{ kJ/mol}$
 DG° for the overall reaction is:

- A) -8.8 kJ/mol .
- B) -7.1 kJ/mol .
- C) -5.4 kJ/mol .
- D) $+5.4 \text{ kJ/mol}$.
- E) $+8.8 \text{ kJ/mol}$.

4. The standard reduction potentials (E°) for the following half reactions are given. (B)

Fumarate + 2H^+ + $2\text{e}^- \rightleftharpoons$ succinate $E^\circ = +0.031 \text{ V}$
 $\text{FAD} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{FADH}_2$ $E^\circ = -0.219 \text{ V}$

If you mixed succinate, fumarate, FAD, and FADH_2 together, all at 1 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 FADH₂ would become reduced.
- B) Fumarate would become reduced, FADH₂ 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, FADH₂ would be unchanged because it is a cofactor.

5. 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: (E)

- A) Malate + NAD⁺ ® oxaloacetate + NADH + H⁺.
- B) Malate + NADH + H⁺ ® oxaloacetate + NAD⁺.
- C) NAD⁺ + NADH + H⁺ ® malate + oxaloacetate.
- D) NAD⁺ + oxaloacetate ® NADH + H⁺ + malate.
- E) Oxaloacetate + NADH + H⁺ ® malate + NAD⁺.

6. Consider the reaction: A + B ® 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 (DG°) for the reaction? Describe the relationship between K_{eq} and DG° .

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

7. Explain in quantitative terms the circumstances under which the following reaction can proceed.

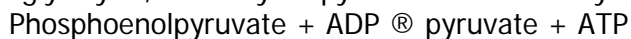


Ans: A reaction for which DG° is positive can proceed under conditions in which DG is negative. From the relationship

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

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 DG can then have a negative value.

8. In glycolysis, the enzyme pyruvate kinase catalyzes this reaction:



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



$DG^\circ = -30.5$ kJ/mol



$DG^\circ = -61.9$ kJ/mol

Ans: The reaction is the sum of reaction 2 and the reverse of reaction 1. Therefore, $DG^\circ = -31.4 \text{ kJ/mol}$.

$$\begin{aligned} DG^\circ &= -RT \ln K_{\text{eq}}' \\ \ln K_{\text{eq}}' &= -DG^\circ / RT \\ &= 31.4 \text{ kJ/mol} / [(8.315 \text{ J/mol}\cdot\text{K})(298 \text{ K})] \\ \ln K_{\text{eq}}' &= 12.672 \\ K_{\text{eq}}' &= 3.19 \times 10^5 \end{aligned}$$

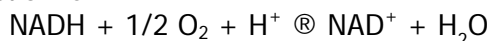
9. What is an oxidation? What is a reduction? Can an oxidation occur without a simultaneous reduction? Why or why not?

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.

10. If DE° for an oxidation-reduction reaction is positive, will DG° be positive or negative? What is the equation that relates DG° and DE° ?

Ans: Negative. $DG^\circ = -n \mathfrak{F} DE^\circ$.

11. During transfer of two electrons through the mitochondrial respiratory chain, the overall reaction is:



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

Ans: $DG^\circ = -n \mathfrak{F} DE^\circ$

For reactions involving NADH, two electrons are transferred ($n = 2$). So $DG^\circ = (-2)(96.48 \text{ kJ/V}\cdot\text{mol})(1.14 \text{ V}) = -220 \text{ kJ/mol}$.