### Table 4.3

**Thermo. of Metabolism pp135-138:** Like Problem S1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0'$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-Glucose + ATP $\rightarrow$ d-glucose-6-phosphate + ADP</td>
<td>$-16.7$</td>
</tr>
<tr>
<td>d-Glucose-6-phosphate $\rightarrow$ d-fructose-6-phosphate</td>
<td>$+1.7$</td>
</tr>
<tr>
<td>d-Fructose-6-phosphate + ATP $\rightarrow$</td>
<td>$-14.2$</td>
</tr>
<tr>
<td>d-fructose-1,6-diphosphate $\rightarrow$</td>
<td></td>
</tr>
<tr>
<td>Fructose-1,6-diphosphate $\rightarrow$ dihydroxyacetone phosphate + glyceraldehyde-3-phosphate</td>
<td>$+23.8$</td>
</tr>
<tr>
<td>Dihydroxyacetone phosphate $\rightarrow$ glyceraldehyde-3-phosphate</td>
<td>$+7.5$</td>
</tr>
<tr>
<td>Glyceraldehyde-3-phosphate + phosphate + NAD$^+$ $\rightarrow$</td>
<td></td>
</tr>
<tr>
<td>1,3-diphosphoglycerate + NADH + H$^+$</td>
<td>$+6.3$</td>
</tr>
<tr>
<td>1,3-Diphosphoglycerate + ADP $\rightarrow$ 3-phosphoglycerate + ATP</td>
<td>$-18.8$</td>
</tr>
<tr>
<td>3-Phosphoglycerate $\rightarrow$ 2-phosphoglycerate</td>
<td>$+4.6$</td>
</tr>
<tr>
<td>2-Phosphoglycerate $\rightarrow$ phosphoenolpyruvate + H$_2$O</td>
<td>$+1.7$</td>
</tr>
<tr>
<td>2-Phosphoenolpyruvate + ADP $\rightarrow$ pyruvate + ATP</td>
<td>$-31.4$</td>
</tr>
<tr>
<td>Pyruvate + NADH + H$^+$ $\rightarrow$ lactate + NAD$^+$</td>
<td>$-25.1$</td>
</tr>
<tr>
<td>Pyruvate $\rightarrow$ acetaldehyde + CO$_2$</td>
<td>$-19.8$</td>
</tr>
<tr>
<td>Acetaldehyde + NADH + H$^+$ $\rightarrow$ ethanol + NAD$^+$</td>
<td>$-23.7$</td>
</tr>
</tbody>
</table>

*An important reaction in many of these steps is the hydrolysis of ATP: ATP + H$_2$O $\rightarrow$ ADP + phosphate. $\Delta G^0' = -31.0$ kJ mol$^{-1}$. $\Delta H^0' = 24.3$ kJ mol$^{-1}$. Source: C. K. Mathews and K. E. van Holde, 1990, Biochemistry (Redwood City, Calif.: Benjamin/Cummings).
Find $\Delta G^0'$ for the HYDROLYSIS of D-glucose-6-phosphate

\[ \text{d-Glucose} + \text{ATP} \rightarrow \text{d-glucose-6-phosphate} + \text{ADP} \quad -16.7 \]

Reverse the above and add it to the ATP equation

\[ \text{d-glucose-6-phosphate} + \text{ADP} \rightarrow \text{d-Glucose} + \text{ATP} \quad +16.7 \]

\[ \text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate} \quad -31.0 \]

\[ \text{d-glucose-6-phosphate} + \text{H}_2\text{O} \rightarrow \text{d-Glucose} + \text{phosphate} \quad -14.3 \]

The first step of burning glucose is add a phosphate to the 6 position. This is a very uphill reaction, as can be seen for the $\Delta G^0'$ when coupled to hydrolysis of ATP. Half of the -31 kJ/mol is used to put on the phosphate!

But, ATP **CANNOT** drive this reaction **WITHOUT** an enzyme that **COUPLES** the two reactions.

*No reaction will happen by putting ATP + glucose in water without enzyme for many years!*
I made up these numbers, but it must be something like this.

**COUPLING MECHANISM**

\[
\begin{align*}
G + P & \rightarrow G6P + H_2O & \Delta G^\circ_{KJ/mol} & +14 \\
ATP + H_2O & \rightarrow ADP + P + H^+ & -31 \\
G + P-P-P-A & \rightarrow G6P + P-P-A + H^+ & -17
\end{align*}
\]

A REASONABLE MECHANISM:

\[
\begin{align*}
E + G + PPPA & \rightarrow E-G...PPPA & \Delta G^\circ & -6 \\
E-G-PPPA & \rightarrow E-G-P...PPA & -6 \\
E-G-P...PPA & \rightarrow E + G-P + PPA + H^+ & -17
\end{align*}
\]
Thermodynamics of Metabolism pp135-138

Adapted from D.A. Harris, Bioenergetics at a Glance; Blackwell, Oxford 1995
A more easily “Reduced Species”

“... transport protons across the **inner mitochondrial membrane**, in a process called **chemiosmosis**. This generates potential **free energy** in the form of a **pH** gradient and an **electrical potential**...”

-about 1000 mitrochondria /cell x 10^{14} cells in body = approx 10^{17} mitrochondria in our bodies. **They cycle ~100 lbs of ADP----> ATP---->ADP per day.**
CITRIC ACID CYCLE (where the NADH comes from)
Similar to Cytochrome C

Myoglobin

(a)

either $\text{Fe}^{3+}$ (ferric) or $\text{Fe}^{2+}$ (ferrous)
Reading for Monday: Chapter 7: pp 241-247 (Electrochemistry)

**Why Electrochemistry in this course??:**
Useful work (w_{other}) from harnessing electron transfer reactions

These *voltages* are merely another way to express Gibbs Free Energy
Electrons from $\text{H}_2(\text{g})$ spontaneously go from negative to positive potential.

Standard Reduction Potentials

$\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{NADH}$

$\text{Ubiquinone = CoQ}$

$\text{Cytochrome c}$

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2 \text{O}$
**Electrochemistry:** Harnessing electron transfer reactions

Consider: \( \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s) \)

\[ \Delta G^0 = -214 \text{ kJ/mol} ; \] What will happen?

![Diagram showing electron flow from Zn to Cu](image)

**on left:** electrons flow from Zn to Cu

But, only a little tiny bit. Why?

**Answer:** + charge builds up in Zn and electrons can’t get out.
Consider $\text{Zn}(s) + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu}(s)$

Make the electrons go the long way around and grab on to them

negative charge builds up

has HIGH resistance

salt bridge
max (reversible) Volts = J/coulomb is a measure of $\Delta G$

$$\Delta G = -T \Delta S_{\text{univ}} + w_{\text{useful}}$$

at const $T$, $P$

for reversible process: $-T \Delta S_{\text{univ}} = 0$ (as current $\rightarrow 0$)

$$\Delta G = w_{\text{useful}, \text{rev}} = -nF\xi = \text{coulombs x volts} = \text{MAX useful work}$$

where $n =$ moles of electrons and $F = -96500$ coulombs/mol

$$\xi = \text{equilibrium voltage in J/coulomb}$$

$$\xi = \Delta G/(-nF)$$

$$\xi^0 = -\Delta G^0/(nF) = \text{STANDARD REDUCTION POTENTIAL}$$