Each question is worth 2 points – Good luck!

1. The protein phosphatase-1 enzyme (PP1) is phosphorylated by activated protein kinase
A. PP1 is more active once phosphorylated. During glucagon-stimulated glycogen breakdown in the liver, does this mode of regulation make sense? Why?

2. Brazil has been growing large batches of yeast for over 30 years in bio-reactors in order to reduce their dependence on foreign oil—they use the generated ethanol as an additive to gasoline, which burns better and cleaner than most grades of gasoline. (The down side is that the production of the sugars for this process has contributed to deforestation in Brazil.)

A. What must be absent from the bioreactors for the production of ethanol to proceed efficiently?

B. Very recently, the DNA of these bio-reactor yeast cultures was sequenced and compared to the genome in lab strains. Strikingly, the yeast had mutated to express extra copies of the genes required to make thiamine pyrophosphate from vitamin B6. Write out the reaction that requires this cofactor in yeast, which you think was critical for these cultures to thrive. Be sure to include the full names of the reactants and products and the name of the enzyme.
3. Draw the α-D-pyranose form of glucose, and indicate with an arrow which carbon is released as CO₂ in the oxidative phase of the pentose phosphate pathway:

![Diagram of glucose metabolism]

4. In which cellular compartment are you most likely to find the following molecule?

5. Give the name of the metabolite that would most likely immediately build-up in cells treated with:

   A. malonate:

   [Diagram of malonate metabolism]

   B. fluoroacetate:

   [Diagram of fluoroacetate metabolism]

   C. caffeine

   [Diagram of caffeine metabolism]

6. A major target of insulin, which we have not discussed, is the transcriptional repression of the gene encoding phosphoenolpyruvate carboxykinase. Draw the structures of the reactants and products for this enzyme (any molecules other than carbohydrates can be abbreviated):

   ![Diagram of enzyme structure]
Does it "make sense" that insulin activates phosphoenolpyruvate carboxykinase?

7. Use the following table to calculate the $\Delta E^\circ$ for the delivery of 2 electrons from the following molecule to NAD.

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$</td>
<td>0.815</td>
</tr>
<tr>
<td>Fe(II) + e^- \rightarrow Fe(III)</td>
<td>0.771</td>
</tr>
<tr>
<td>NO$_2^-$ + 2H$^+$ + 2e$^-$ \rightarrow NO$_2$ + H$_2$O</td>
<td>0.421</td>
</tr>
<tr>
<td>Cytochrome f (Fe(III)) + e$^-$ \rightarrow cytochrome f (Fe(II))</td>
<td>0.365</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$ (ferriyanide) + e$^-$ \rightarrow Fe(CN)$_6^{4-}$</td>
<td>0.36</td>
</tr>
<tr>
<td>Cytochrome a$_3$ (Fe(III)) + e$^-$ \rightarrow cytochrome a$_3$ (Fe(II))</td>
<td>0.35</td>
</tr>
<tr>
<td>O$_2$ + 2H$^+$ + 2e$^-$ \rightarrow H$_2$O</td>
<td>0.298</td>
</tr>
<tr>
<td>Cytochrome a (Fe(III)) + e$^-$ \rightarrow cytochrome a (Fe(II))</td>
<td></td>
</tr>
<tr>
<td>Cytochrome c (Fe(III)) + e$^-$ \rightarrow cytochrome c (Fe(II))</td>
<td>0.294</td>
</tr>
<tr>
<td>Cytochrome c$_1$ (Fe(III)) + e$^-$ \rightarrow cytochrome c$_1$ (Fe(II))</td>
<td>-0.359</td>
</tr>
<tr>
<td>Cytochrome b (Fe(III)) + e$^-$ \rightarrow cytochrome b (Fe(II))</td>
<td>0.077</td>
</tr>
<tr>
<td>Ubiquinone + 2H$^+$ + 2e$^-$ \rightarrow ubiquinol + H$_2$</td>
<td>0.943</td>
</tr>
<tr>
<td>Fumarate$^{2-}$ + 2H$^+$ + 2e$^-$ \rightarrow succinate$^{2-}$</td>
<td>0.331</td>
</tr>
<tr>
<td>2H$^+$ + 2e$^-$ \rightarrow H$_2$ (at standard conditions, pH 0)</td>
<td>0.000</td>
</tr>
<tr>
<td>Cr(III)-Cp + 2H$^+$ + 2e$^-$ \rightarrow butyl-Cp</td>
<td>0.000</td>
</tr>
<tr>
<td>Oxaloacetate$^{2-}$ + 2H$^+$ + 2e$^-$ \rightarrow malate$^{2-}$</td>
<td>-0.166</td>
</tr>
<tr>
<td>Pyruvate$^-$ + 2H$^+$ + 2e$^-$ \rightarrow lactate$^-$</td>
<td>-0.185</td>
</tr>
<tr>
<td>Acetaldehyde + 2H$^+$ + 2e$^-$ \rightarrow ethanol</td>
<td>-0.197</td>
</tr>
<tr>
<td>RAD + 2H$^+$ + 2e$^-$ \rightarrow RADH$_2$</td>
<td>-0.210*</td>
</tr>
<tr>
<td>Glutathione + 2H$^+$ + 2e$^-$ \rightarrow 2 reduced glutathione</td>
<td>-0.23</td>
</tr>
<tr>
<td>S + 2H$^+$ + 2e$^-$ \rightarrow H$_2$S</td>
<td>-0.214</td>
</tr>
<tr>
<td>Lipase acyl + 2H$^+$ + 2e$^-$ \rightarrow dihydroxyacid</td>
<td>-0.29</td>
</tr>
<tr>
<td>NAD$^+$ + H$^+$ + 2e$^-$ \rightarrow NADH</td>
<td>-0.320</td>
</tr>
<tr>
<td>NAD$^+$ + H$^+$ + 2e$^-$ \rightarrow NADPH</td>
<td>-0.324</td>
</tr>
<tr>
<td>Acetoacetate + 2H$^+$ + 2e$^-$ \rightarrow $\beta$-hydroxybutyrate</td>
<td>-0.346</td>
</tr>
<tr>
<td>$\alpha$-ketoglutarate + CO$_2$ + 2H$^+$ + 2e$^-$ \rightarrow isocitrate</td>
<td>-0.38</td>
</tr>
<tr>
<td>2H$^+$ + 2e$^-$ \rightarrow H$_2$ (at pH 7)</td>
<td>-0.414</td>
</tr>
<tr>
<td>Farnesin (Fe(III)) + e$^-$ \rightarrow farnesin (Fe(II))</td>
<td>-0.432</td>
</tr>
</tbody>
</table>

8. Assuming that Faraday's constant is 100 kJ/(Volts • mol), how many ATPs—in theory—could be generated from the delivery of these 2 electrons in question #7?
9. The following portion of a polymer forms what molecule?

\[ \text{Diagram of polymer structure} \]

10. Some evidence suggests that the \( \beta \) and \( \gamma \) subunits associated with G protein coupled receptors may also be important for hormone-dependent signaling.

A. In one publication, the released \( \beta \) subunit was found to directly activate a chloride channel that is expressed in kidneys. Let's say that the activated \( \alpha \) subunit is involved in opening a water channel, which acts in parallel to the chloride channel. What do you think the GAP is for this process?

B. Name one way that the \( \alpha \) subunit of a G protein might become constitutively activated (not including genetic mutations):

11. Would the following events lead to (A) higher or (B) lower levels of circulating fats in the bloodstream?

A. removal of the gallbladder

B. a perilipin mutant protein that cannot be phosphorylated

C. a constitutively activated form of PKA in adipocytes
12. What is the full name of the electron acceptor for the following reactions (no abbreviations):

A.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_{14} \text{CH}_3 & - \text{OH}_2 - \text{C} - \text{O} - \\
& \text{S-CoA} \\
\downarrow & 2e^-
\end{align*}
\]

\[
\text{CH}_3(\text{CH}_2)_{14} \text{CH}_3 - \text{CO}-\text{CH}_2 - \text{C} - \text{O} - \\
& \text{S-CoA}
\]

B.

\[
\begin{align*}
\text{CH}_2\text{OH} & - \text{O} - \text{CH}_2 - \text{OH} - \\
& \text{H} - \text{CH}_2 - \text{OH} - \\
& \text{H} - \text{OH} - \\
& \text{H} - \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} & - \text{O} - \text{CH}_2 - \text{OH} - \\
& \text{H} - \text{OH} - \\
& \text{H} - \text{OH} - \\
\end{align*}
\]

\[
\begin{align*}
2e^- \\
\end{align*}
\]

13. After diacyl glycerol is generated from the action of phospholipase C, there is a kinase that acts on this molecule and that is required to generate a precursor for the regeneration of PIP$_2$. Draw the structure of the product the reaction catalyzed by this kinase:
14. The change in free energy for hexokinase and phosphofructokinase-1 is essentially identical, yet PFK-1 is more highly regulated. Why do you think this is?

15. What is the name of the following molecule and where are you most likely to find it in the cell?

\[
\begin{align*}
&\text{CH}_3 \\
&\text{CH}_2-N-\text{CH}_3-\text{CH}-\text{CH}_2-\text{COO}^- \\
&\text{CH}_3 \quad \text{OH}
\end{align*}
\]

16. A naturally occurring mutant form of apolipoprotein CII was examined. In which type of particle do you find this apolipoprotein?

Interestingly, individuals expressing the mutant exhibited lower levels of the gene encoding an enzyme that oxidizes stearoyl-CoA, which normally makes an important cellular lipid. Draw the reaction that you think might be catalyzed by this enzyme:
17. Draw the reaction—including the structures of the reactant(s) and product(s)—that represents the most unfavorable reaction in glycolysis:

18. The generation of ketone bodies is accelerated in response to fasting. Draw the structure of one of the two ketone bodies that is an acid and state its name:

19. Into which metabolic enzyme that we discussed might the breakdown products (i.e., loss of NH$_3$) of each of the following molecules be delivered? (Please write the full name of the enzyme...)

   A.  
   
   $H_2N-C\text{H}_2-CO_2H$

   B.  
   
   $\text{CO}_2\text{H}$
   $	ext{CH}_2$
   $	ext{CH}_2$

   $H_2N-\text{C}\text{H}-CO_2\text{H}$
20. Which vitamin is needed for the following reaction?

21. Draw the structures of the reactants and the products of the reaction catalyzed by fructokinase (please draw the structure of the product in the furanose conformation):

22. The $\Delta G^\circ$ for the hydrolysis of phosphate from a singly phosphorylated form of fructose is $\sim -16$ kJ/mol. What is the standard free energy change for the reaction catalyzed by fructokinase?
23. The following is an intermediate in the reaction catalyzed by which enzyme?

\[ \text{structure image} \]

24. The complete oxidation of glucose generates 6 molecules of carbon dioxide. Name the enzymes that catalyze the release of CO₂ from carbohydrates during this process:

25. Assuming that each NADH generates 3 ATPs and each FADH₂ generates 2 ATPs, how many ATPs would be made by the complete oxidation of the following molecule?

\[ \text{structure image} \]
26. A scientist fed radioactive molecules of inorganic phosphate into the reaction catalyzed by glyceraldehyde-3-phosphate dehydrogenase. What is the name of the enzyme in the glycolytic pathway that would remove this radioactive molecule and transfer it to ADP via a substrate level phosphorylation?

27. An increase in the activity of phosphofructokinase-2 would have what effect on glycolysis?

HAVE AN AWESOME AND WELL-DESERVED SPRING BREAK!!!