1. (20 pts) Thermodynamics
(a; 5 pts) Starting from two of the equations above, show that \( \Delta G < 0 \) when \( Q < K \) for a reaction.

\[
\Delta G = \Delta G^0 + RT \ln Q
\]

\[
\Delta G = -RT \ln K_{eq}^1
\]

\[
\Delta G = -RT \ln K_{eq}^1 + RT \ln Q
\]

So if \( Q < K \),

\[
\frac{\ln Q}{K_{eq}^1} < 0 \text{ and } \Delta G < 0
\]

\[
\Delta G = RT \ln \left( \frac{Q}{K_{eq}^1} \right)
\]

Score for the page 16
(b; 5 pts) Circle all of the true statements below (i)-(ii)-(iii). Explain your reasoning.

(i) \( \Delta G^\circ \) for each step of an operational biochemical pathway must be negative. \[ \text{[ ]} \]

(ii) \( \Delta G \) for each step of an operational biochemical pathway must be negative. \[ \text{[ ]} \]

(iii) \( K_{eq} \) for each step of an operational biochemical pathway must be \( 1 \). \[ \text{[ ]} \]

The actual free energy change \( \Delta G \) must be \( < 0 \) for the flux for each reaction to be in the forward direction – if a reaction \( \Delta G > 0 \) the net flow will be backward or zero.

(c; 10 pts) The biochemical standard state free energy changes for phosphoenolpyruvate (PEP) hydrolysis and ATP hydrolysis are as follows:

\[
\text{ATP + H}_2\text{O} \rightleftharpoons \text{ADP + P}_i + \text{H}^+ \quad \Delta G^\circ = -30.5 \text{ kJ/mole at 298 K} \\
\text{PEP + H}_2\text{O} \rightleftharpoons \text{pyruvate + P}_i \quad \Delta G^\circ = -61.9 \text{ kJ/mole at 298 K}
\]

Calculate \( K_{eq} \) at 298 K for the phosphorylation of ADP by PEP to give ATP + pyruvate. Remember that because we are assuming pH 7, the concentration (formally, the activity) of \( \text{H}^+ \) relative to its standard state is 1. (The activity of water is also taken as 1.)

\[ \text{PEP + ADP + H}^+ \rightleftharpoons \text{ATP + pyruvate} \quad K_{eq} = ? \]

Add reaction, reversing the first one

\[ \text{ADP + P}_i + \text{H}^+ \rightleftharpoons \text{ATP} + \text{H}_2\text{O} \quad \Delta G^\circ = +30.5 \text{ kJ/mole} \]

\[ \text{PEP + H}_2\text{O} \rightleftharpoons \text{pyruvate} + \text{P}_i \quad \Delta G^\circ = -61.9 \text{ kJ/mole} \]

\[ \text{PEP + ADP + H}^+ \rightleftharpoons \text{ATP + pyruvate} \quad \Delta G^\circ = -31.4 \text{ kJ/mole} \]

\[ K_{eq} = e^{-\Delta G^\circ / RT} = e^{-(-31400 \text{ J/mole})/(8.314 \text{ J/mole} \cdot 298 \text{ K})} \]

\[ (b; \Delta G^\circ = -RT \ln K_{eq}) = e^{(31400/(8.314 \times 298))} = e^{12.67} \approx 3.18 \times 10^5 \]

Score for the page 15
2. (20 pts) Protein Structure
The sequence KSTG is found within the solvent-exposed N-terminal tail of the DNA packaging protein Histone H3, and it is frequently modified during gene regulation.

- Draw the structure of \((\text{OAc-K})(\text{P-S})\text{TG}\), which is KSTG with the Lysine being acetylated at the \(\varepsilon\)-amino group and the Serine being phosphorylated.
- Assume all trans peptide bonds, give correct stereochemistry for C-\(\alpha\)'s, and identify the chiral side chain carbon; you don't need to draw the correct stereochemistry at that carbon.
- The pK_\text{a}'s of the phosphate in P-Ser are about 2 and 6. The pK_a of the N-terminal \(-\text{NH}_3^+\) is 8. In your diagram, show the P-Ser in its predominant form at pH 8.

- Estimate the average total charge on the peptide at pH 8: \(-2.5\) \(+3\)

- Estimate the charge of the unmodified KSTG peptide at pH 8: \(+0.5\) \(+2\)

\[\text{pK}_a = 2, 6 \text{ so deprotonated}\]

\[\text{Chemin pH 8 } (=\text{pK}_a \text{ for N-terminal } -\text{NH}_3^+)\]

\[+\frac{1}{2} \quad 0 \quad -2 \quad -1\]

For KSTG:

\[+\frac{1}{2} \quad +1 \quad 0 \quad -1\]

Score for the page \(120\)
3. (20 pts) Carbohydrates

The disaccharide trehalose, \( O-\alpha-D\text{-glucopyranosyl-(1\rightarrow1)-}\alpha-D\text{-glucopyranose} \), has a variety of biological functions in different organisms. For example, trehalose is used for energy storage in insect flight muscle, which have the highest power output (energy produced per unit time) of any tissue. The glycosidic linkage is hydrolyzed by the enzyme trehalase.

- Draw a Haworth projection and a physically reasonable chair structure for trehalose. Number the carbons.
- Speculate on why trehalose might be used in preference to glycogen in insect flight muscle.
- List two other essential functions of carbohydrates besides their use as fuel.

Score for the page 120
4. (25 pts) Secondary Structure in Proteins

- List the two essential structural characteristics of stable secondary structures discussed in class.

- Sketch the hydrogen bonding pattern in a parallel β sheet, showing five residues of each of two strands. Show α carbon stereochemistry. Represent side chains as R. Don't write too large!

- On your diagram, circle the four atoms that define the Phi (Φ) torsion angle for any one residue and the four atoms that define Psi (Ψ) for another residue.

- Based on your picture, explain why β sheet structures are found in the upper left of the Ramachandran diagram (one sentence will do, not a trick question).

- Name a program used for 3-D visualization of biomolecules.

- All N-bond valences satisfied for backbone

- Any side chain (except Pro) can be accommodated

+4

N→C

N→C

 för peptide
för parallel
för H-bonding pattern
för stereochemistry
för Φ
för Ψ

+2

Nick R groups on same side

+4 The β-sheet is nearly an extended structure, so Φ and Ψ are in the neighborhood of -180, +180 (≈ -120, +120)

Pymol, Rasmd, Jmol, Molmod, 
Kingrid, Kinemage etc.

Score for the page 125
5. (15 pts) Lipids and Redox
Consider oleic acid vs. stearic acid. The table gives their structures, densities, and standard enthalpies of combustion, $\Delta H^\circ_c$, essentially a measure of caloric content.

<table>
<thead>
<tr>
<th></th>
<th>Oleic Acid, $C_{18}H_{34}O_2$</th>
<th>Stearic Acid, $C_{18}H_{36}O_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td><img src="image" alt="Oleic Acid Structure" /></td>
<td><img src="image" alt="Stearic Acid Structure" /></td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>0.895 g/ml</td>
<td>0.941 g/ml</td>
</tr>
<tr>
<td>$\Delta H^\circ_c$</td>
<td>$-11161$ kJ/mol</td>
<td>$-11291$ kJ/mol</td>
</tr>
</tbody>
</table>

- Explain why oleic acid has a lower density than stearic acid.
- Explain why oleic acid has a lower heat of combustion than stearic acid, and why both of them have larger heats of combustion per carbon atom than glucose ($\Delta H^\circ_c = -2805$ kJ/mol).

- Oleic acid has a lower density (greater volume per molecule) because the $C\equiv C$ d.i.b. means that the chains cannot pack as efficiently as the straight-chain saturated alkyl group. The 2 $H$'s would reduce only a $\sim 1\%$ difference in mass vs. an $5\%$ change in density.

- Stearic acid is fully reduced so there are two more $e^-$. Available to give to $O_2$ than there are in oleic acid.

$18\text{ Stearic acid }C\text{'s have total } \# = -32, \text{ gives up } 104\text{ e}^- \text{ in mol of } CO_2$

$18\text{ Oleic acid }C\text{'s } \# = -30, \text{ gives up } 102\text{ e}^- \text{ in mol of } CO_2$

- The 18 carbons in glucose have an average oxidation of 0

So they can only give up $4\text{e}^-$ per carbon to $O_2$ as opposed to $\frac{104}{18} \approx 6$ for the lipids.

"Give up fewer electrons is fine"