1. (15 pts) Thermodynamics

(a; 5 pts) What is the origin of the hydrophobic effect (at least at room temperature and below)? What is the sign of $\Delta S$ for dissolving a nonpolar solute like octane in water?
(b; 4 pts) The free energy change for a process is given by $\Delta G = \Delta G^\circ + RT\ln Q$. Why is it especially important for biochemists to be able to calculate $\Delta G$, whereas chemists are often content to just use the fact that $\Delta G^\circ = -RT\ln K$?

(c; 6 pts) Give an example of an endothermic dis-ordering process, specify the signs of $\Delta H$ and $\Delta S$, and describe the temperature dependence of the process.
2. (24 pts) Peptide Structure
(a; 12 pts) Draw the structure of the dipeptide (phospho-Y)C disulfide-linked to the dipeptide CR. Draw the predominant ionic form at pH 7. The pKa’s of protonated phosphotyrosine are about 2 and 5.8. The pKa’s for protonated C- and N-termini are about 3 and 8. Assume all trans peptide bonds, and give correct stereochemistry for Cα’s.

(b; 12 pts) Fill in the table for the charge of the peptide above, to the nearest integer or half-integer. You do not need a calculator.

<table>
<thead>
<tr>
<th>pH</th>
<th>0</th>
<th>3</th>
<th>7</th>
<th>10</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From your table, without doing any more calculations, specify a range for the possible pI of the peptide and give your reasoning.

Why is the pI important for protein separation procedures?

Why does the cytoplasm have to be a reducing environment?

Score for the page__________
3. **(15 pts) Lipids and Carbohydrates**
   (a; 5 pts) Sketch the structural aspect of a lipid molecule that determines whether it will form a micelle vs. a lipid bilayer. How does *cis*-unsaturation in the lipid chain increase membrane fluidity (or cause lipids of the same molecular weight to be liquids rather than solid)?

   (b; 4 pts) Give two reasons that fat packs more dietary calories per gram than carbohydrates.

   (c; 6 pts) What are the three functions of carbohydrates that we discussed? Name carbohydrate-containing molecules that carry out each of the three functions.
4. **(36 pts) Secondary Structure in Proteins**

(a; 4 pts) What was the point of drawing the simple lattice models for the compaction of chains into small areas (volumes)?

(b; 4 pts) List the two essential structural characteristics of stable secondary structures discussed in class.

(c; 8 pts) Draw a Newman projection for $\psi(\Psi) = -90^\circ$, with the C\(\alpha\) being the forward end of the bond that is going straight into the page for the Newman projection. Explain why $\psi$ values between about $-90^\circ$ and $-150^\circ$ are a forbidden region of the Ramachandran diagram.

(d; 4 pts) Sketch a picture explaining the direction and structural origin of the macrodipole of the alpha helix.
(e; 8 pts) We emphasized the idea of “sidedness” of alpha helices and beta sheets. **Why is this important in protein folding?**

For the two sequences below, identify which one is more likely to be two strands of a beta sheet:_________ and which one is more likely to be an alpha helix:_________.

**Sketch how each one exhibits sidedness – either draw a picture or add labeling to make your point.**

(1) PELAKVARTLDQMLLENLAGA

(2) WRFSINVDAPGLSICWKYSM
(f; 8 pts) On the extended polypeptides below, sketch in the H-bonding pattern of the parallel beta sheet. Sketch on the picture how and why the backbone is deformed out of the plane to make the pleated sheet conformation. Label the R groups and draw in H bonds on the pleated picture at the bottom.

Score for the page____________
5. **(10 pts) Buffers**

(a; 2 pts) Calculate the pH for a solution of acetic acid/Na acetate composed of 50 mM HOAc and 50 mM NaOAc. The pKa of acetic acid (HOAc) is 4.75.

(b; 3 pts) Adding 10 mM HCl will give 60 mM HOAc and 40 mM OAc\(^{-}\). What is the new pH?

(c; 2 pts) Adding an additional 31 mM HCl will give 91 mM HOAc and 9 mM NaOAc. What is the new pH?

(d; 3 pts) What will the pH after the addition of a further 10 mM HCl? [Hint: HCl will be in excess, which we assume will completely suppress the dissociation of HOAc.]