Problem Set 1: Solution Key

Total time required ~50 min (If you take more than twice this time, there is likely an issue regarding how you are approaching the problem, please seek help).

Calculate – use a formula to give quantitative answers.

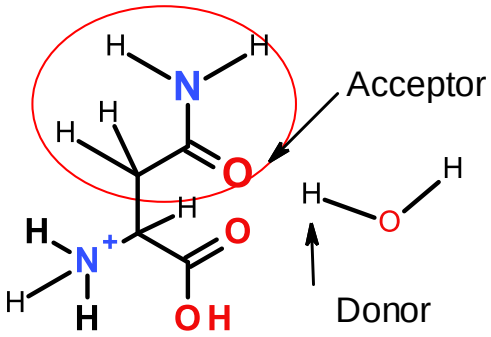
Sketch - you need not calculate the curve, just try to reproduce its general features. However, take care in representing certain 'landmarks', such as inflection points, etc. Fully label the axis with units and scale.

Unless instructed otherwise, please include plots or sketches with your problem set, the graphs should have:

i) Brief title

ii) The axis labeled, with units if appropriate

iii) If there are multiple datasets on the same plot they should be clearly distinguished using a legend.



1. (5 points, 10 min) The structure shown to the right is that of the amino acid asparagine.

   a) Add any protons that may be missing from this structure. You can assume that the ionizable groups are fully protonated, as indicated on the diagram (2 pts).

   Add hydrogens so that carbon has four bonds. Nitrogen 3 (unless +1 charge = protonated), then four. Oxygen 2 (unless -1 charge = deprotonated).

   b) Circle the atoms that are unique to asparagine (the sidechain atoms). What is the name of the functional group on the sidechain? (1 pt) See diagram. The functional group is an amide.

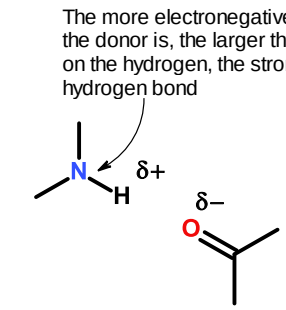
   c) Add one H_2O molecule to your drawing that donates a H-bond to the **sidechain** of asparagine. Clearly label the hydrogen bond donors and acceptors (2 pts).

   [Draw the waters as "H-O-H", with approximate bond angles and bond lengths.]

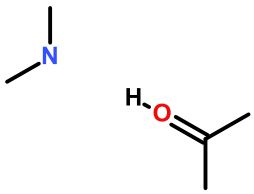
2. (4 pts, 5 min) What is the electronic configuration of the most stable form of Ca? Is it ionized and if so what is its charge? Briefly justify your answer. Calcium has 20 electrons, so its electronic configuration would be: 1s – 2e, 2s – 2e, 2p – 6 e, 3s – 2 e, 3p – 6 e, 4s – 2e

If Ca loses the two electrons from the 4s orbital it will have the same electronic configuration as argon, which is stable. So, the most stable form of the Ca ion is Ca^{+2}

3. (5 points, 5 min) Rank, from highest to lowest, the hydrogen bond strength of the following groups; assume the H-bond acceptor is the carbonyl (C=O) group. a) -N-H b) -O-H c) –S-H d) -C-H. Briefly justify your answer. [Hint: A table of electronegativities may be helpful, see lecture 2 notes. The electronegativity of S is 2.58]. Since the energy of a hydrogen bond is mostly (90%) due to electrostatic interactions between the partial positive charge on the hydrogen and the partial negative change on the acceptor, the electronegativity of the atoms should be a good predictor of the strength. Since the acceptor is the same (C=O) we only need to consider how the partial charge changes on the H for each donor. The order of hydrogen bond strength (most energy released when the bond is formed) follows the electronegativity: OH, NH, SH, CH. The CH would be very weak, such that it generally would not be considered to form H-bonds, and OH would form the strongest.



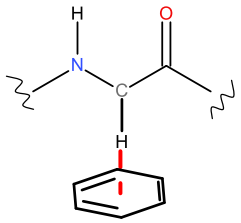
Correct arrangment of atoms in a hydrogen bond



Incorrect arrangement:
- the nitrogen is only forming two bonds
- the oxygen is forming three.

Note that in a hydrogen bond, the hydrogen is **not** transferred from the donor to the acceptor. The donor provides the hydrogen that participates in the hydrogen bond. The hydrogen remains attached to its electronegative donor. For example, the left side of the diagram is a correct representation of a hydrogen bond in secondary structure, the right side is clearly incorrect.

4. (5 pts, 10 min) The interaction shown on the right is often observed in protein structures, where the Cα-H group is positioned above the middle of an aromatic ring, as drawn on the right. What features of this interaction lead to its stability? Be sure that you discuss the role of all the atoms on the amino acid.



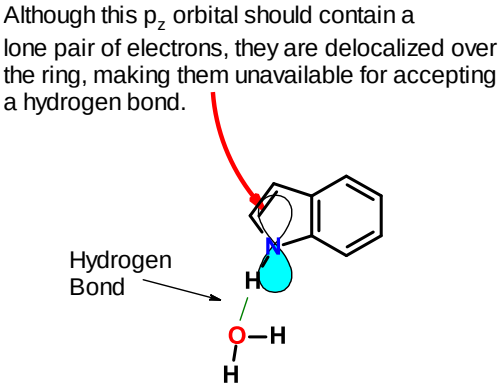
This is a type of hydrogen bond that doesn't follow the X-H Y rule.

In this case, the electronegative "Y" atom are the delocalized electrons above the plane of the aromatic system, these act as the hydrogen bond acceptor. Normally, a C-H group is not sufficiently polarized to result in a stable H-bond, however in this case the a-carbon is interacting with 2 electronegative atoms (N & O) that will withdraw electrons from it. This will make the a-carbon withdraw more electron from the H, so the partial positive charge on the H is larger than you would find in a normal C-H bond.

5. (5 pts, 10 min) Open the JSmol page associated with this problem set. In order to answer this question, you will have to look at the structures of amino acids that are given in lecture 5 of OLI.

a) Draw the chemical structure that is displayed in JSmol (2 pts).

See diagram



b) State whether the compound shown in JSmol is polar or non-polar (or both); briefly justifying your answer (2 pts). It is both, the larger 6 membered ring could participate in non-polar interactions while the NH group on the five-membered ring is polar. Note that it can only donate a hydrogen bond, because the lonepair on the nitrogen (which could normally accept an H-bond) is delocalized, as illustrated on the diagram.

c) What amino acid contains this functional group (1 pt)? Tryptophan

6. (6 pts, 15 min) Use Excel to determine the best linear fit to the following data points.

[S] mM	V (uM/sec)
0	0.00
1	1.15
2	2.10
5	3.80

a) Submit a chart with your problem set that has the following features (2 pts):
   i) The data where the points are indicated by filled circles and they are not connected by a line.
   ii) The linear fit is on the chart, shown as a dotted line.
   iii) The chart has a title "Enzyme Velocity"
   iv) The x- and y-axis are labeled appropriately.
   v) the range for the x-axis is 1-5.

   See plot on right.

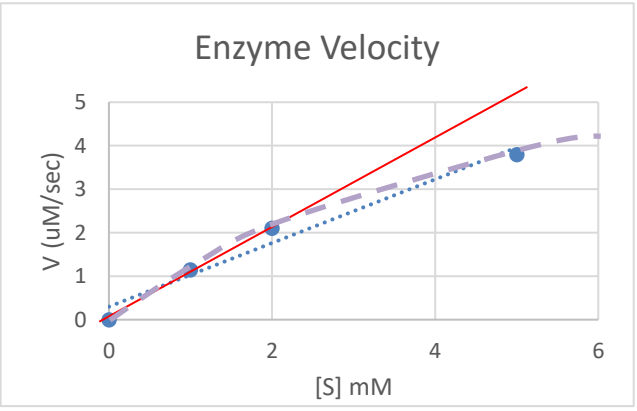


Figure 1. Plot of enzyme velocity versus substrate concentration. Best fit line is v = 0.73 [S] + 0.30

b) In the legend to the figure, include a brief description of the plot and the values for the equation of the line (2 pts) See plot on right. Note that the variable in the equation in the legend are the variable (v and [S]) not the generic "x" and "y"

c) Do you feel that the data is well fit to a straight line? Justify your answer (2 pts).

It is actually difficult to tell without one or more of the following:

i) the error in the data

ii) more data points at higher concentration.

Assuming that the error in the data is small, then the first three points look like they fall on one line, and the fourth point falls below the line. The best linear fit to the first three points is shown as the red line. This equation does not predict the last point very well, suggesting that the data is better fit to another function. The dashed purple line shows the data fit to $v = v_o [S]/(K_M + [S])$.