Some constants and equations that may be useful:

\[ K_w = [H^+][OH^-] = 1 \times 10^{-14} \]
\[ K_a \text{ for the formation of carbonic acid from carbon dioxide and water} = 0.003 \ (K_w) \text{ at 37°C} \]
\[ K_a = [H^+][\text{A}^-]/[\text{HA}] \]
\[ \text{pH} = \text{pK}_a + \log [\text{A}^-]/[\text{HA}] \]
\[ K_a \text{ for H}_3\text{PO}_4 = 7.5 \times 10^{-3} \]
\[ K_a \text{ for H}_2\text{PO}_4^- = 1.38 \times 10^{-7} \]
\[ K_a \text{ for HPO}_4^{2-} = 3.98 \times 10^{-13} \]
\[ K_a \text{ for acetic acid} = 1.74 \times 10^{-5} \]
\[ K_a \text{ for formic acid, CH}_2\text{O}_2 = 1.78 \times 10^{-4} \]
\[ K_a \text{ for lactic acid, C}_3\text{H}_6\text{O}_3 = 1.41 \times 10^{-4} \]

Multiple choice: 10 questions, worth 2 points each. Circle all of the correct answers. Some questions may have more than one correct answer.

1. The three-dimensional structure of macromolecules is formed and maintained primarily through non covalent interactions. Circle all of the non covalent interactions.
   A) carbon-carbon bonds
   B) hydrogen bonds
   C) hydrophobic interactions
   D) ionic interactions
   E) London Dispersion
   F) None of these

2. What functional groups are present on this molecule?
   A) ether, ketone and amine
   B) alcohol, phenyl, alkene and amide
   C) amide, alcohol, phenyl and ketone
   D) alcohol, alkene, phenol and amide
   E) ketone, alcohol, amine, alkene, phenyl

3. Diastereomers are: (circle all of the correct statements):
   A) Superimposable mirror images of each other
   B) Non superimposable mirror images of each other
   C) Enantiomers.
   D) Stereoisomers with more than one chiral center
   E) None of these

4. How many different stereoisomers can this molecule have?
   A) 4
   B) 2
   C) 32
   D) 16
   E) None of these, the correct number of stereoisomers is______

5. If the free energy change $\Delta G$ for a reaction is 20.56 kJ/mol, the reaction is:
   A) endergonic.
   B) endothermic.
   C) exergonic.
   D) exothermic.
   E) at equilibrium
5. Enzymes are biological catalysts that enhance the rate of a reaction by:
A) decreasing the activation energy.
B) decreasing the amount of free energy released.
C) increasing the activation energy.
D) increasing the amount of free energy released.
E) increasing the energy of the transition state

6. Buffers
I. neutralize solutions
II. contain a weak acid and its conjugate base
III. contain a weak acid and a base
IV. maintain the pH of the solution close to the -log of the $K_a$ of the weak acid.

A) I, II and III  B) I and III  C) II and IV  D) IV only  E) none of these

7. Which of the following is true about hydrogen bonds? Circle all of the true statements.
A) Hydrogen bonds are shorter and stronger than covalent bonds.
B) The geometry of a water molecule results in the unequal sharing of electrons
C) Hydrogen bonds must involve at least one water molecule.
D) Polar molecules are insoluble in water because they can form hydrogen bonds with water molecules.
E) None of these

8. Osmosis is water movement across a semi-permeable membrane. Which of the following is true about water movement across cell membranes? Circle all of the true statements
A) In a hypotonic solution, cells will shrink.
B) In an isotonic solution, cells will shrink.
C) In a hypertonic solution, cells will shrink.
D) Cells can neither shrink nor swell because water cannot penetrate the plasma membrane.
E) There is an increase in enthalpy.
F) None of the above statements are true.

9. Micelles are characteristic of what type of molecules:
A) charged  C) polar  E) non polar
B) amphipathic  D) amphiprotic

10. A dynamic steady state results when
A) there is no net energy transfer
B) an organism is at equilibrium with its surroundings.
C) there is no net energy transfer.
D) the rate of intake or synthesis of a molecule equals the rate of its disappearance.
E) None of these, or more than one of these, circle all correct answers.

Short answer section, 4 questions worth 3 points each:

11. (3 points) How does carbonic acid anhydrase affect the equilibrium of the bicarbonate buffer system?

12. (3 points) A kilodalton is 1000 daltons. What is the definition of a dalton? What are kD used to measure?
13. (3 points) Why is SDS added to polyacrylamide to purify proteins?

Problem section. Show all of your work. No work= no points.

15. (10 points) A 67 year old, 50 kg female is brought into the ER. The patient is awake and breathing very rapidly (panting) and is very agitated. Dr. House orders blood gases and blood pH to be determined. The results of the tests indicate that the patient has metabolic acidosis. Dr. House is old and can not remember a thing from his Chemistry classes, so now you need to help him save his patient.

<table>
<thead>
<tr>
<th>Normal values</th>
<th>Patient values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.4</td>
<td>pH 7.2</td>
</tr>
<tr>
<td>HCO₃⁻ 24 mM</td>
<td>CO₂ 1.0 mM</td>
</tr>
<tr>
<td>CO₂ 1.2 mM</td>
<td></td>
</tr>
</tbody>
</table>

a. What effect does breathing rapidly (panting) have on blood pH? Explain.

b. Determine the amount of bicarbonate (mM) in the patient’s blood.

c. How much bicarbonate should be administered to this patient. Her total blood volume is 4.5L. The bicarbonate is supplied in ampules (little glass vials) that contain 1mEq (milli-equivalent) per mL. Each ampule has 25 mEq. For bicarbonate, 1mmole = 1 mEq. How many vials of bicarbonate should be given to this patient?

16. (10 points) If 300 mL of a 0.2 M phosphate buffer at pH 7.5 has a new pH of 6.9 after some volume of 0.18 M hydrochloric acid was added, what volume of 0.18 M hydrochloric acid was added?
15. (16 points) Draw the titration curve for the titration of 20 mL of a 0.18 M solution of arginine (pKa$_1$ = 2.17, pKa$_2$ = 10.989.04) with 0.12 M sodium hydroxide. Clearly label the axes of your graph in mL of sodium hydroxide added. Be sure to include pH values and volumes for the following: Start of the titration (no sodium hydroxide added), the pH at the volume that is half of the volume of each endpoint, pH and volume at the end points of the titration. Show all of your calculations.
17. (5 points) Acetylcholine is a neurotransmitter that is degraded by acetylcholinesterase to form acetic acid and choline, as shown below. If a 5 mL sample of acetylcholine at pH 7.42 was incubated with acetylcholinesterase and the new pH was 6.97, determine the number of moles of acetylcholine present in the 5 mL sample.

18. (10 points) Draw the structure for the tetrapeptide, LPYW, that predominates at pH=7.

19. (10 points) What is the pI for the tetrapeptide, DQKF? The pKa for the carboxy terminus is 3.2, the pKa for the amino terminus is 8.1.
20. (3 points) The following peptide was cleaved with chymotrypsin. What are the products?

**CANKCWIIWILDCARD**

21. (3 points) The following three peptides were purified by cation exchange chromatography at pH 5. All amino terminus pKa values are 8, all carboxy terminal pKa values are 3:

<table>
<thead>
<tr>
<th>DETRIDT</th>
<th>ANGELS</th>
<th>WASHINGTON</th>
</tr>
</thead>
</table>

a. Which peptide eluted first?
b. Second?
c. Third?

22. (4 points) List the reagents for the following reactions that involve a peptide with "n" amino acids (n = the number of amino acids in the peptide):

a. Peptide\(_{(n)}\) ---\(\rightarrow\) labelled amino acid + free amino acids

b. Peptide\(_{(n)}\) ---\(\rightarrow\) labelled amino acid + peptide \(_{(n-1)}\)