Chem 464
Biochemistry

Multiple choice (4 points apiece):

1. An allosteric interaction between a ligand and a protein is one in which:
   A) binding of a molecule to a binding site affects binding of additional molecules to the
   same site.
   B) binding of a molecule to a binding site affects binding properties of another site on the
   protein.
   C) binding of the ligand to the protein is covalent.
   D) multiple molecules of the same ligand can bind to the same binding site.
   E) two different ligands can bind to the same binding site.

2. One of the enzymes involved in glycolysis, aldolase, requires Zn$^{2+}$ for catalysis. Under
   conditions of zinc deficiency, when the enzyme may lack zinc, it would be referred to as the:
   A) apoenzyme.
   B) coenzyme.
   C) holoenzyme.
   D) prosthetic group.
   E) substrate.

3. The concept of “induced fit” refers to the fact that:
   A) enzyme specificity is induced by enzyme-substrate binding.
   B) enzyme-substrate binding induces an increase in the reaction entropy, thereby
   catalyzing the reaction.
   C) enzyme-substrate binding induces movement along the reaction coordinate to the
   transition state.
   D) substrate binding may induce a conformational change in the enzyme, which then
   brings catalytic groups into proper orientation.
   E) when a substrate binds to an enzyme, the enzyme induces a loss of water (desolvation)
   from the substrate.

4. When the linear form of glucose cyclizes, the product is a(n):
   A) anhydride.
   B) glycoside.
   C) hemiacetal.
   D) lactone.
   E) oligosaccharide.

5. Which of the following statements about starch and glycogen is false?
   A) Amylose is unbranched; amyllopectin and glycogen contain many ($\alpha 1 \rightarrow 6$) branches.
   B) Both are homopolymers of glucose.
   C) Both serve primarily as structural elements in cell walls.
   D) Both starch and glycogen are stored intracellularly as insoluble granules.
   E) Glycogen is more extensively branched than starch.
6. The DNA oligonucleotide abbreviated pATCGAC:
   A) has 7 phosphate groups.
   B) has a hydroxyl at its 3’ end.
   C) has a phosphate on its 3’ end.
   D) has an A at its 3’ end.
   E) violates Chargaff’s rules.

7. When double-stranded DNA is heated at neutral pH, which change does not occur?
   A) The absorption of ultraviolet (260 nm) light increases.
   B) The covalent N-glycosidic bond between the base and the pentose breaks.
   C) The helical structure unwinds.
   D) The hydrogen bonds between A and T break.
   E) The viscosity of the solution decreases.

Essay Questions 10 points each

8. What are ‘R states’, and ‘ T states’, and what do these states have to do with the binding of oxygen to hemoglobin?

   T state - ‘tense’- low affinity - form seen when hemoglobin is in the deoxygenated state.
   R state - ‘relaxed’ - high affinity - form seen when oxygen is bound to hemoglobin.

   Used to explain the sigmoidal binding curve of oxygen to hemoglobin. When oxygen is abundance, hemoglobin shift to the high affinity form, and binds oxygen more tightly. As the hemoglobin goes into the peripheral tissue and the concentration of oxygen is reduced, the hemoglobin shifts to a low affinity form, and releases oxygen more easily.

9. Below is a possible mechanism for thermolysin, a proteolytic enzyme. Point out all the different kinds of catalysis that the enzyme is using to make this reaction go faster. You may assume that there are additional interactions that help to stabilize the intermediate state, that were no shown in this diagram.

   The diagrams show that Zn^{2+} is part of the reaction mechanism, indicating metal ion catalysis.

   In step 1 the Glu 143 act as a base to remove a proton from water to create a hydroxide ion, so this would be general base catalysis

   The hydroxide ion then attacks the substrate, so this would be specific base catalysis.

   In step 3 His 231 donates a proton to the transition state, so this would be general acid catalysis.

   The final two points is for transition state stabilization, indicated in the question itself.
10. Discuss the different ways that can be used to regulate the activity of an enzyme. (Hint: first try to list as many different ways that enzyme activity can be regulated, then give a 1-2 sentence description of how the regulation works)

(Up to 5 points if you do a good answer for a different question)

Allosteric regulation
Binding of other small molecules that either increase or decrease the Km or Vmax of an enzyme.

Reversible covalent modification
Adding or removal of phosphates or several other moities that can increase or decrease the Km or Vmax of an enzyme

Irreversible covalent modification
Proteolytically cleaving an enzyme with a specific protease to activate the enzyme

Often any or all of the above control mechanisms can be combined in the control of a single enzyme

11. I told you that you should be able to draw the structure of glucose both in the linear form and in the ring form with α and β anomers. Do that now. Now for the challenging part. Galactose is an epimer of Glucose because it has the opposite configuration at the 4’ C in the sugar chain. Use this information to draw the structure of Galactose in the linear, and ring form with α- and β-anomers. Now for the 3 point bonus challenge. Glucose is roughly 2/3 β and 1/3 α. Do you think the same is true for Galactose? Why or why not? EXPLAIN.

Since the 4’ OH of galactose is on the same side of the ring as the β OH group, I would guess that steric interference would make this form less stable, so the amount of β would decrease.
12. Discuss the different kinds of glycoconjugates observed in biochemistry. (Hint, list in a hierarchical order the different kinds of glycoconjugates, then give a 1-2 sentence explanation of each item in your list.)

From your homework

Glycoconjugates

Proteoglycans - Very large heteropolysaccharides like chondroitin sulfate, heparin sulfate or keratin sulfate are attached to a much smaller (by mass) protein core.

Glycoproteins - smaller, but more structurally complex carbohydrates are attached to larger (by mass) proteins. Commonly differentiated as O linked or N linked depending on how sugar is attached to protein

Glycolipids - a carbohydrate attached to a lipid. One subclass is the ganglioside

13. One nucleic acid that was discussed was cyclic AMP or Adenosine 3',5' cyclic monophosphate. Draw the structure of this molecule. (Yes, I know it is not one of the ones I had you memorize, but the name tells you how to draw it from the things you know!)

14. What are the different ways that DNA can be damaged from things found in the environment. (Hint: List both the damaging agent, and the kind of damage that is done.)

   Ionizing radiation X-rays or gamma rays can break any covalent bond in a DNA structure.
   Near UV light can create thiamine-thiamine dimers in a double stranded DNA
   Nitrous acid or compounds that can be metabolized into nitrous acids greatly accelerate the rate of base deamination
   Alkylating agents like S-Adenosyl methionine or nitrogen mustard add methyl groups to DNA at various locations, and these added methyl groups can interfere with the normal double stranded structure of DNA
   DNA can be easily mutated by oxidative damage caused by free radicals (agents with single electrons). One of the most damaging is the hydroxyl radical.
1 B.
2 A.
3 D
4 C
5 C.
6 B
7 B