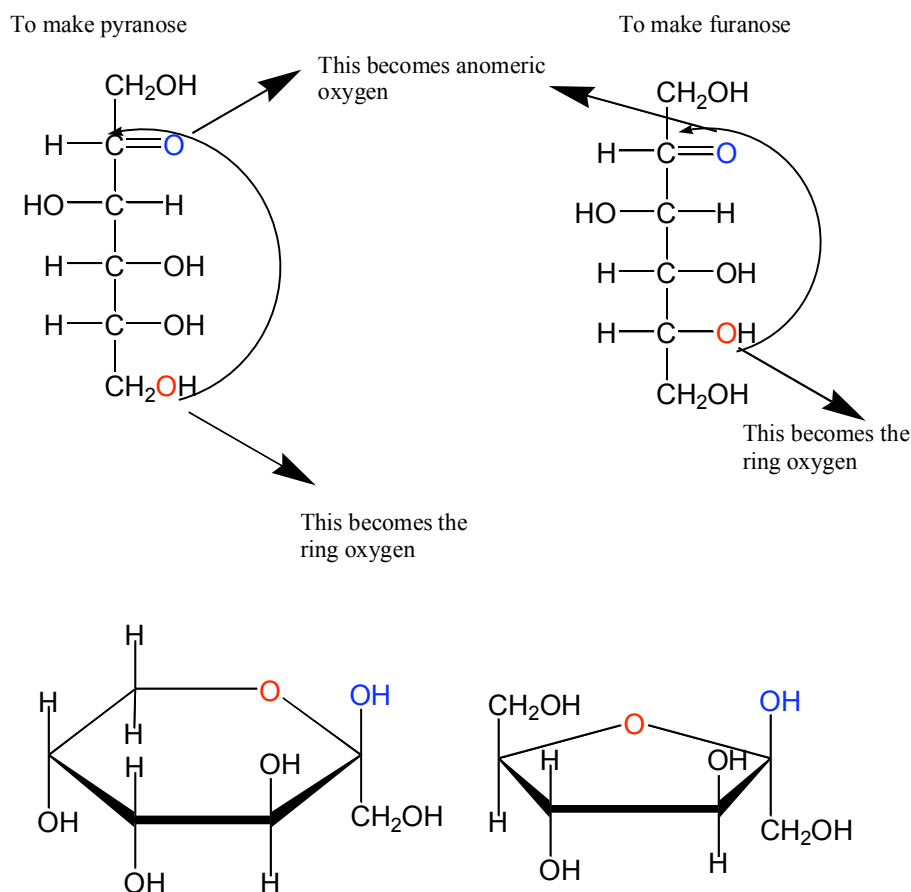


# Answers to Problem Set #6

## BMB 401 Spring 2003

### Problem 1

- There are 3 chiral carbons (carbons 3, 4, and 5).
- Carbon 3 is S. Carbon 4 is R. Carbon 5 is R. Remember that in Fischer projections, the atoms on the horizontal are pointing towards you.
- The number of stereoisomers is  $2^n$ , where n is the number of chiral carbons. Therefore there are 8 stereoisomers.
- 



In both of these cases, you need to transpose the ring structure back to a Fischer projection. When the hydroxyl group at the anomeric carbon is on the same side of a **Fischer projection** as the oxygen atom at the highest numbered asymmetric carbon, the configuration at the anomeric carbon is alpha. For aldohexoses it's easier.

Problem 2 Disaccharides consist of two monosaccharides that are joined covalently by an O-glycosidic bond. This forms only when a hydroxyl group of one sugar reacts with the anomeric carbon of the other.

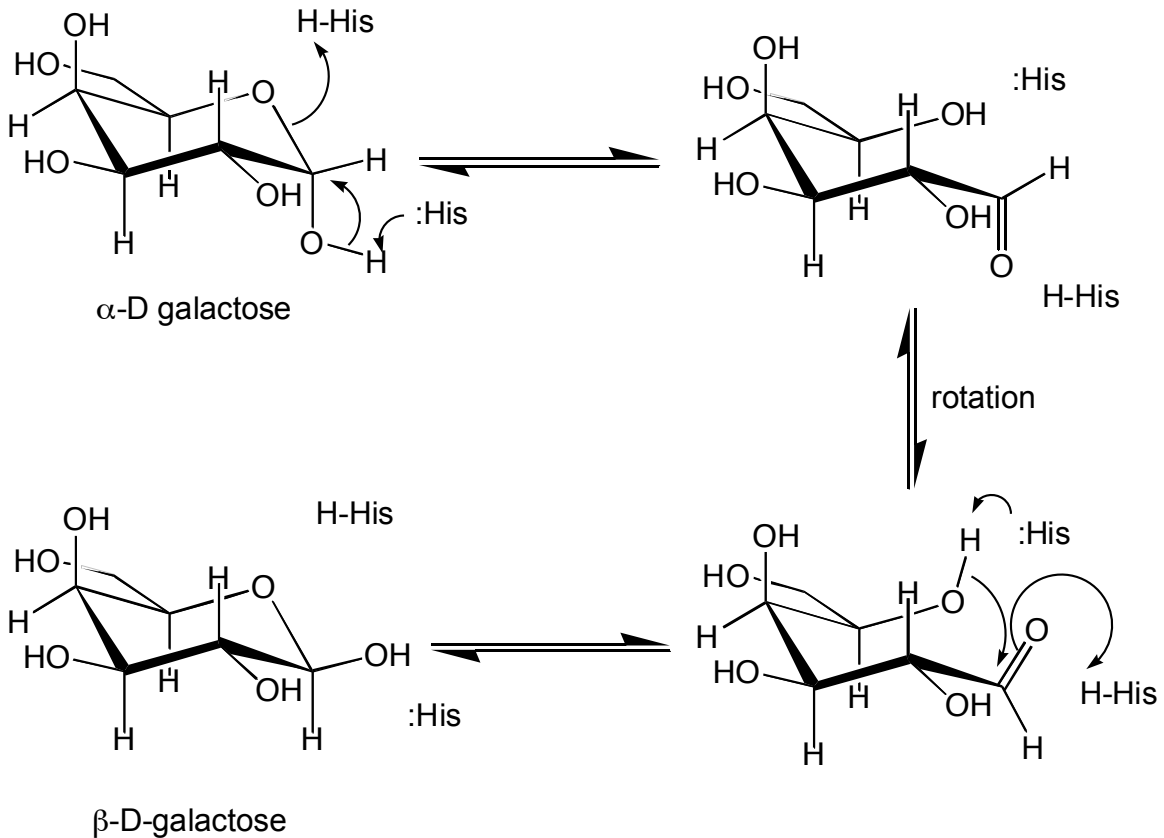
There should be eight galactosides (1-2, 1-3, 1-4, and 1-6) considering both alpha and beta anomers. Remember, that sugars with non-reducing ends have the ending sides rather than oses. Therefore, the terminology galactosides would suggest that galactose would be the first sugar.

There should be eight glucosides for the above reason.

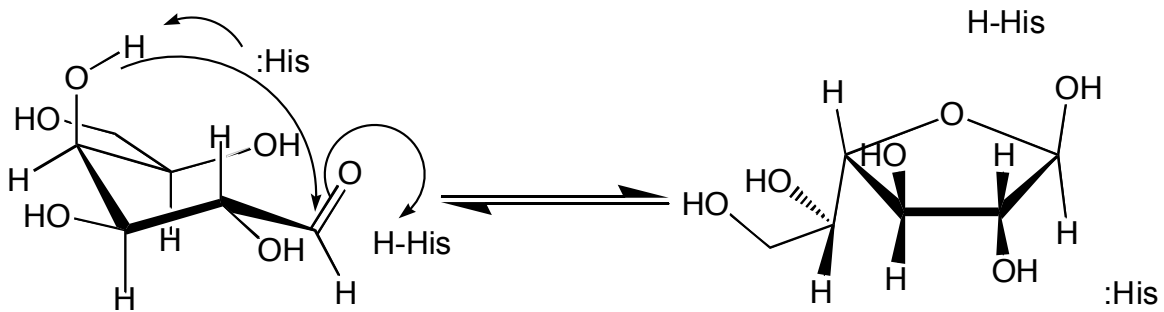
There should be four disaccharides with non-reducing ends. These would all have to be 1-1 linked; however, you need to consider the different anomers. ( $\alpha$ - $\alpha$ ,  $\alpha$ - $\beta$ ,  $\beta$ - $\alpha$ ,  $\beta$ - $\beta$ ).

Therefore, in total, there should be 20 different disaccharides.

Problem 3 In the ring form you cannot invert the configuration at C1 of galactose. However, when the molecule is in the open chain form the inversion is facile. Therefore, the enzyme basically just catalyzes opening of the ring.



In the open chain intermediate, what would happen if the active site histidine accidentally removed the proton of the C-4 hydroxyl rather than the C-5 hydroxyl?

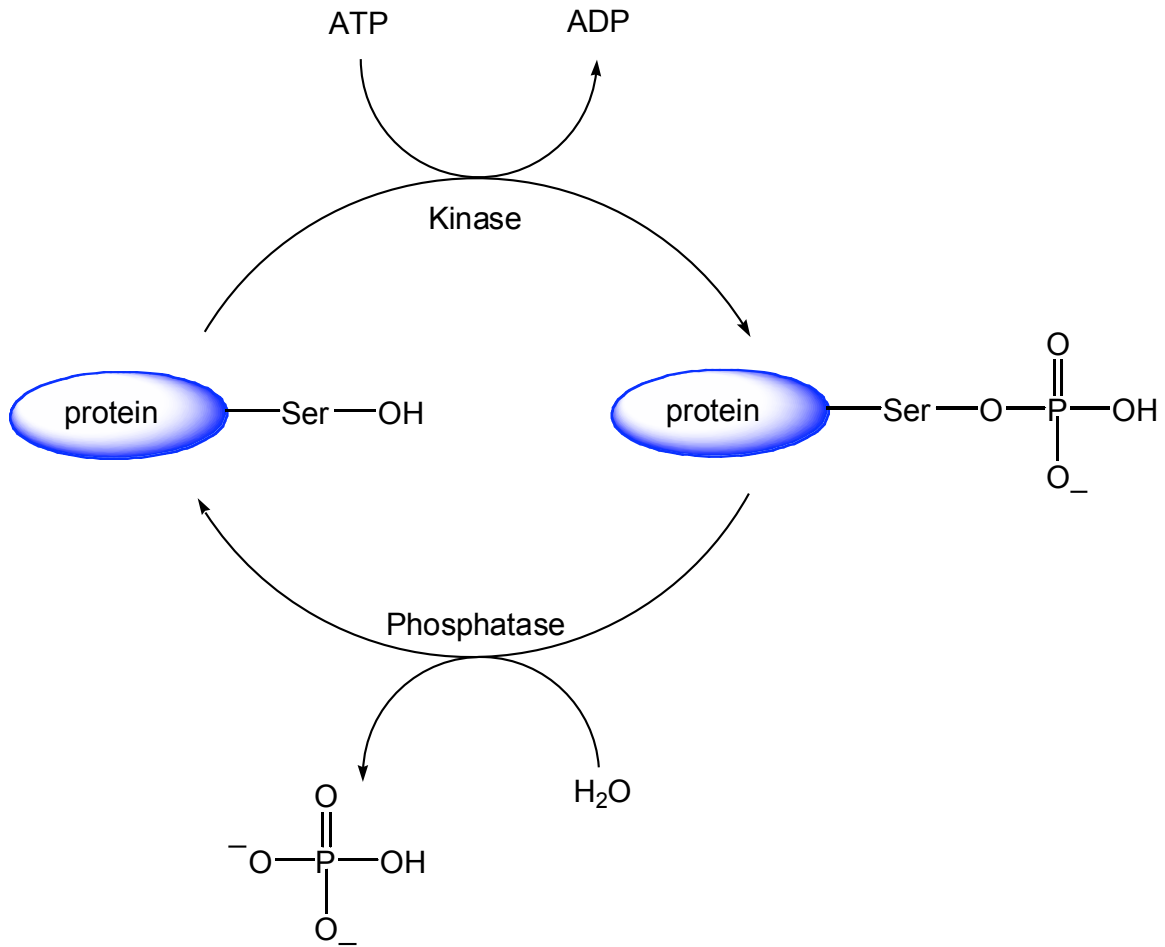


Problem 4 and 6

Look at the pathway drawn in Problem 6. Although each of the amino acids G, J, and H are synthesized from a common precursor, A, the enzymes that are regulated are those that are **committed** to a certain product. Therefore, for the synthesis of J, 7 would be in the first enzyme in that pathway. 6 would be the first enzyme in the pathway that is committed to the synthesis of G, and 9 would be the first enzyme in the pathway that is committed to the synthesis of H. Therefore, J would regulate 7, whereas G would regulate 6 and H would regulate 9. It would make no sense for H or G to regulate 1, 2, 3, because that would inhibit the synthesis of J. By the same token, it would make no sense for G or H to regulate 4, because it would inhibit the synthesis of the other amino acid.

Problem 5

A futile cycle is one in which ATP, the energy currency in the cell, is hydrolyzed non-productively. If the phosphatase activity were significantly higher than the kinase activity, each time the protein is phosphorylated, the phosphoryl group would be hydrolyzed off rapidly, before the phosphorylated protein is able to carry out its function.



Problem 7

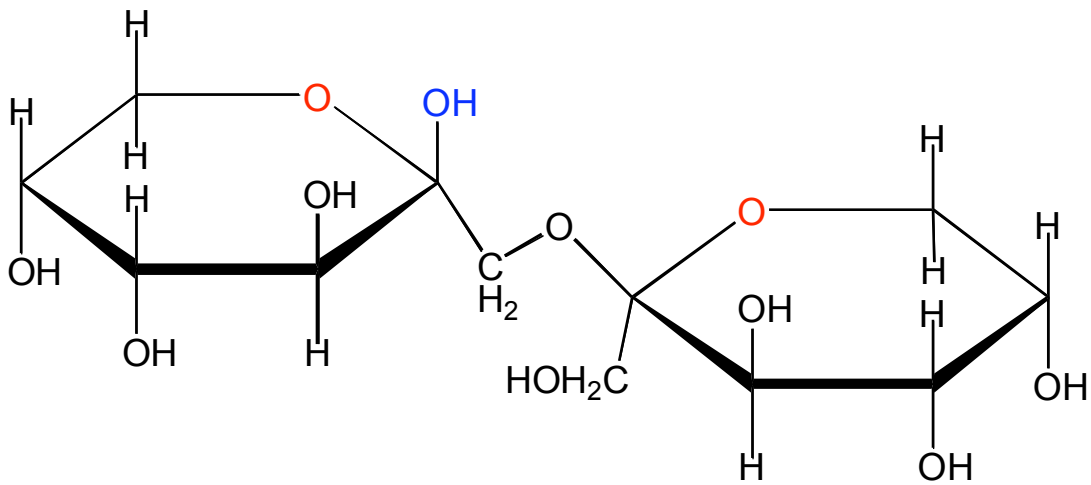
In one particular scenario, ATP could simply bind to a second site that has a higher  $K_d$  than the normal substrate binding site. This site could be a regulatory site that either shuts the enzyme off or dramatically reduces its catalytic efficiency. The higher  $K_d$  would prevent ATP from shutting the enzyme off when ATP is in low abundance.

Problem 8

The chirality of the penultimate carbon of a monosaccharide determines whether the monosaccharide is a D or L sugar.

Problem 9

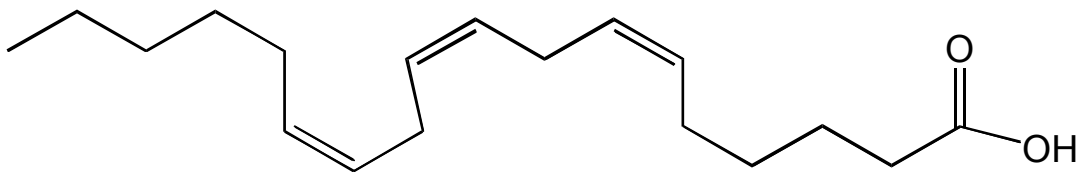
The structure of fructose in its ring form was shown in Problem 1. The most common form is the pyranose form (80%) rather than the furanose form (20%).



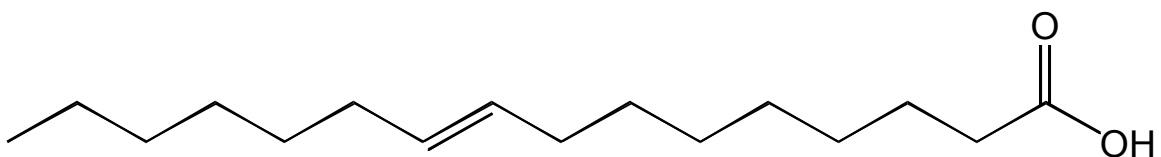
Notice that the beta linkage refers to the sugar on the right, because its configuration is fixed. By contrast, the sugar on the left can open and reclose converting between alpha and beta anomers. It's configuration is thus not stated.

Problem 10      Phosphatidylserine is a more polar molecule (2 possible charges), and would therefore be expected to have the slower nonenzymatic flip-flop motion across a membrane bilayer.

Problem 11      Octadecenoic acid means 18 carbons with one double bond. Octadecatrienoic acid means 18 carbons with 3 double bonds. The 6, 9, and 12 refer to the positions of the double bonds, counting from the carboxylate group. All bonds are cis unless specified.



Problem 12



- Problem 13                      Stearic acid groups are completely saturated, whereas oleic acid groups have one cis double bond. Remember that cis double bonds impart a kink in fatty acid chains, which don't allow them to pack or interact maximally through van der Waals forces. Therefore, they undergo phase transition at lower temperatures.
- Problem 14                      Membranes are dynamic structures. Many important cellular processes take place at the membrane. Although they are composed primarily of phospholipids, other types of hydrophobic molecules are also present. These include proteins, non-phospholipids, and steroid molecules like cholesterol. In addition, polysaccharides can be connected to the surface of membrane-bound proteins, or can be connected to lipids via different types of connecting head groups.
- Problem 15                      The major difference between gram positive and gram negative bacteria is that gram negative bacteria have two phospholipids bilayer structures instead of one. The region between the two phospholipids bilayers is the periplasmic space, which is where the peptidoglycan layer is found. The outer monolayer of the outer bilayer contains antigenic lipopolysaccharides. Gram positive bacteria contain only one phospholipid bilayer. Their peptidoglycan layer is significantly thicker than that of gram negative bacteria. **The crosslink between the relevant lysine of the peptidoglycan chain and D-alanine of an adjacent chain has a 5-glycine spacer (gram positive). The crosslink is directly between lysine and (OR A LYSINE-LIKE MOLECULE) D-alanine in gram negative bacteria.** The outer monolayer of the membrane of gram positive bacteria has antigenic teichoic acids.