Exercise 2:
Carbohydrates

Question 1:

Which of the following statements are TRUE, and which are FALSE? Why?

a. Carbohydrates are exclusively composed of C, H and O atoms with an overall formula $C_nH_{2n}O_n$.

b. Carbohydrates always have one or more chiral centers and different number of epimeric carbons.

c. Carbohydrates can form linear or branched polymers through hydrolysis reaction.

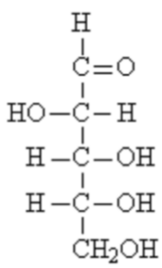
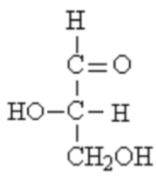
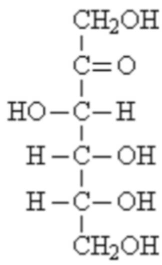
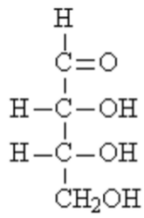
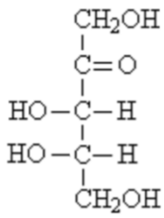
d. Carbohydrates can form complex molecules by covalent binding to proteins, lipids, and nucleotide bases.

e. The primary type of non-covalent interaction in the majority of carbohydrates are hydrogen bonds.

f. sp3-hybridized carbons in carbohydrate building blocks make them convert between different states which in turn makes the oligosaccharides and polysaccharides very flexible.

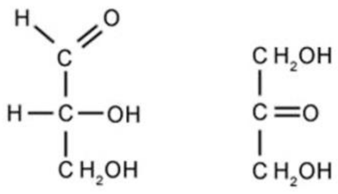
Question 2:

Below you will find linear structures of several monosaccharides. Classify them based on the (1) length of carbon chain, (2) functional group and (3) stereochemistry (handedness).

Question 3:

The smallest monosaccharides are trioses, glyceraldehyde and dihydroxyacetone shown below:



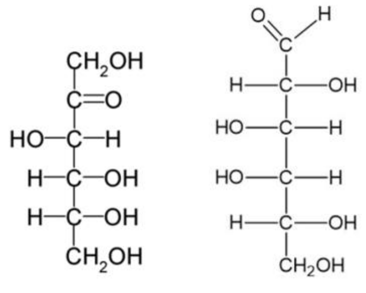
Glyceraldehyde Dihydroxyacetone

a) Can you draw the stereoisomeric versions of each monosaccharide? Include the D- or L-annotation.

b) Can these monosaccharides assemble into cyclic forms in aqeuous solutions? Explain.

Question 4:

Below are the linear structures of D-fructose and D-galactose.



D-Fructose D-Galactose

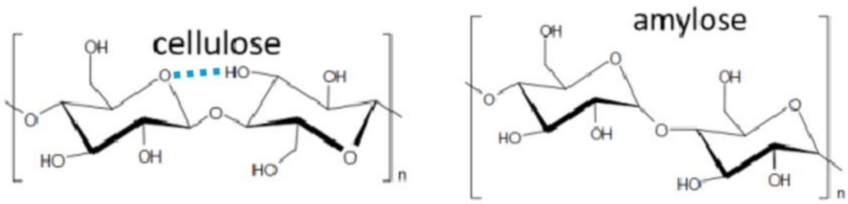
a) Draw the cyclic structures of each sugar in alpha (α) stereoisomeric form and indicate the location of anomeric carbon. How does the beta (β) form differ from the alpha?

b) Lactulose (galatose-β(1→4)β-fructose) is a disaccharide used in the treatment of constipation and hepatic encephalopathy. It is assembled from **1 D-galactose** and **1 D-fructose** building block through **β(1-4)β O-glycosidic linkage**. Draw the structure of this disaccharide based on the cyclic forms of each monosaccharide building block.

c) Melibiulose (galactose-α(1→6)β-fructose) is another disaccharide assembled from the same buidling blocks using the **α(1-6)β O-glycosidic bond**. Draw the structure of this disaccharide based on the cyclic forms of each monosaccharide building block.

Question 5:

Below is a structure of cellulose and amylose chain segments. Both are composed of the same building block (glucose) linked via the same carbon atoms (C1 and C4), but using a **β(1-4)** or **α(1-4)** O-glycosidic linkage. In blue we highlighted the hydrogen bond that is essential for intrachain stability of cellulose leading to assembly into sheets. This improves the mechanical properties of cellulose (making it a great material for cell wall) but excess rigidity of such large polymers reduces the solubility in water.



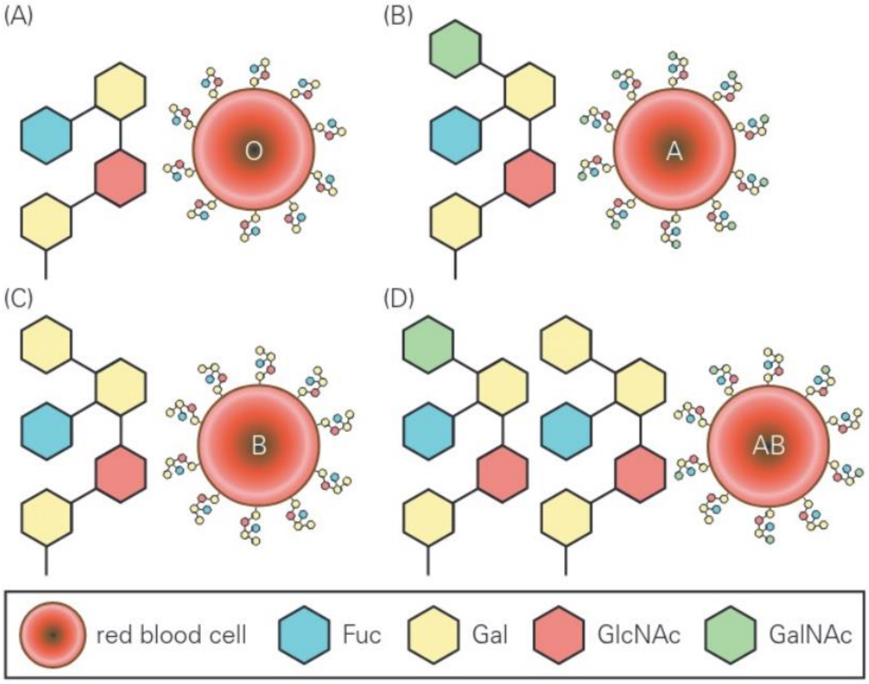
a) What effect does the α(1-4) linkage have on the capacity of amylose to form intrachain hydrogen bonds? How does this influence the macroscopic properties (stability/flexibility and solubility)?

b) Cellulose is often chemically or enzymatically modified to optimize some of its properties. One of the modifications includes the substitution of accessible hydroxyl groups in glucose with negatively charged phosphate groups ($R\text{-}O\text{-}PO_3^{2-}$). What would be the impact of this modification on cellulose packing and mechanical properties? What about the solubility in water?

c) In the above structure of cellulose, label all the hydroxyl groups that can in theory be substituted with phosphate groups (use the sugar ring carbon numbering to label the group locations). Modification of which single group do you think would cause the greatest destabilizing effect? Why?

Question 6:

The O blood type group is known as the universal donor. That means that people having this blood type can give their red blood cells to other people, regardless of their group, without eliciting an immune response (at least to first approximation; more complex in medical practice).



a) Considering the glycosylation pattern of the O blood type versus all other groups, can you explain why that is?

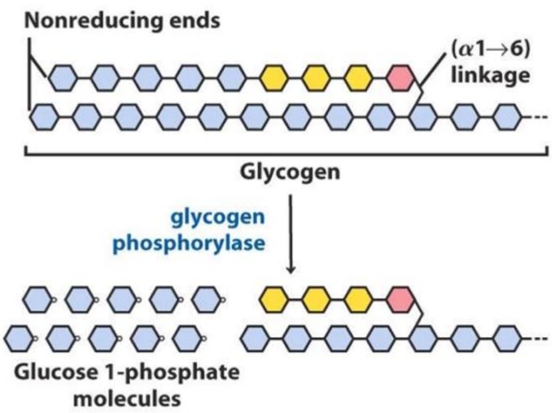
b) Using the same rationale, can you explain why AB group is considered a universal acceptor for red blood cell transfusion purposes?

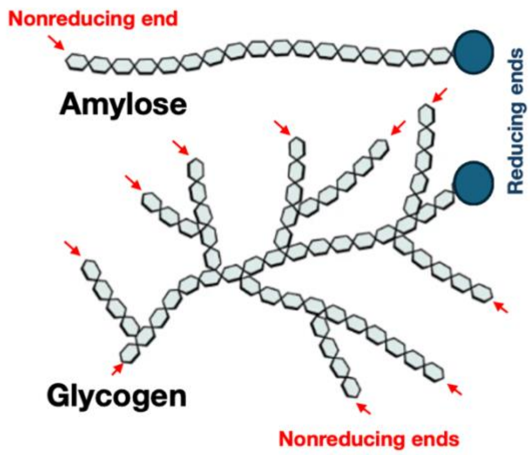
c) If O-type red blood cells can be donated universally, why can't O-type individuals receive blood from any donor?

d) Imagine that you have an endless supply of enzymes to precisely modify carbohydrates on cell surface in any way you wish. How could you use those enzymes to make any red blood cell sample serve as universal donor?

Question 7:

Glycogen phosphorylase is an enzyme that catalyzes the phosphorylation and release of the glucose residue from the termini of glycogen branches ("nonreducing ends", see image below). Assume glycogen phosphorylase can release one molecule of glucose from each nonreducing end in glycogen at a rate of 10 residues per second.





a) If a glycogen molecule has 2'000 nonreducing ends, how many glucose residues can be released per second from this single molecule?

b) If an amylose molecule of the same size has only 1 nonreducing end (no branching), how many glucose residues can be released per second?

c) Calculate the fold-difference in mobilization rate between glycogen and amylose.