Name Key

# Chem 352 - Spring 2018 - Exam II

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1. Honey is an solution of D-fructose and D-glucose monosaccharides. Although when D-fructose is present in polysaccharides it exists mainly in its furanose form, in solution monomeric D-fructose is a mixture of several forms, with β-D-fructopyranose (67%) and β-D-fructofuranose (25%) being the predominant forms.

   a. Draw the Fischer projection for the monosaccharide D-fructose and show, using Haworth projections, how D-fructose can cyclize to form both β-D-fructopyranose and β-D-fructofuranose.

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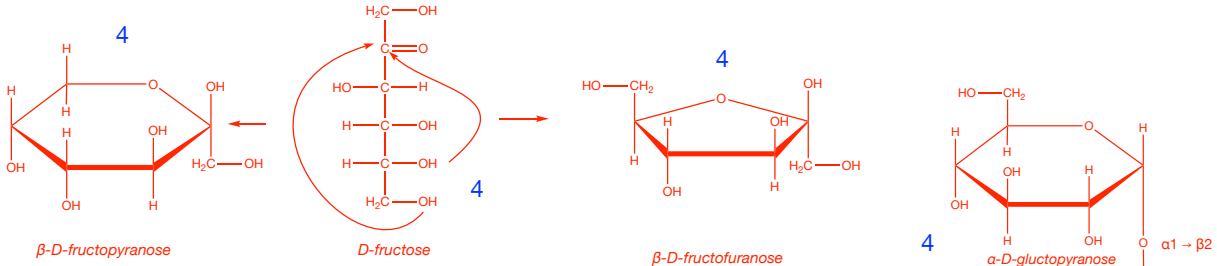


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   b. β-D-fructofuranose is one of the two monosaccharides found in the disaccharide sucrose. Draw the the structure for sucrose.

sucrose

   c. Why can D-fructose be found in multiple cyclic forms as a monomer in solution when it is only found in the β-D-fructofuranose form in the disaccharide sucrose.

As a monomer, the anomeric carbon found in the ring forms of fructose are hemiketals, which are free to open and close and switch to different ring forms. When combined with D-glucose to form sucrose, the anomeric carbon becomes a ketal, which is locked and no longer able to open and close. The ring form of D-fructose that is chosen to form sucrose is enforced by the enzyme that catalyzes the formation of the glycosidic bond between D-frucose and D-glucose 4

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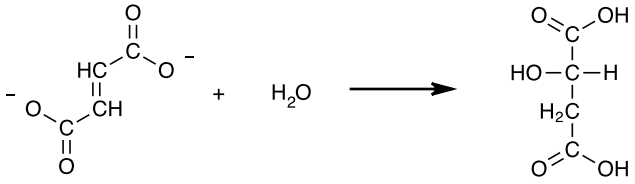
2. One of the steps in the citric acid cycle is the conversion of fumarate to malate. This reaction is catalyzed by the enzyme *fumarase*:




In a kinetics experiment where the fumarase concentration is set at 200 μM, the *turnover number* is observed to be $5.0 \times 10^5$/s and the $K_M$ is observed to be 50 mM.

   a. What is the catalytic rate constant, $k_{cat}$, for this reaction? $5.0 \times 10^5 \frac{1}{s}$ 3
   (*Show your calculations.*)

$k_{cat}$ = turnover number = $5.0 \times 10^5 \frac{1}{s}$

b. What is the expected $V_{max}$ for this reaction? $V_{max} = 100\ \frac{M}{s}$ 3
(*Show your calculations*.)

$$V_{max} = k_2[E]_{total} = k_{cat}[E]_{total} = \left(5.0x10^5\ \frac{1}{s}\right)(200\ \mu M) = 1.0x10^8\ \frac{\mu M}{s}$$

$$V_{max} = \left(\frac{1.0x10^8\ \mu M}{1\ s}\right)\left(\frac{1\ M}{10^6\ \mu M}\right) = 100\ \frac{M}{s}$$

Two reactants and one product, so this is an addition reaction.

c. Which class of *enzyme catalyzed reaction* does fumarase belong to? Lyase 3

d. Under these conditions, does fumarase display "catalytic perfection" No 3
(*Show your calculations*.)

An enzyme displays "catalytic perfection when its catalytic efficiency, in units of 1/M•s, is equal to or greater than $10^8$ 1/M•s.

$$\frac{k_{cat}}{K_M} = \frac{5.0x10^5\ \frac{1}{s}}{50\ mM} = 1.0x10^4\ \frac{1}{mM \cdot s}$$

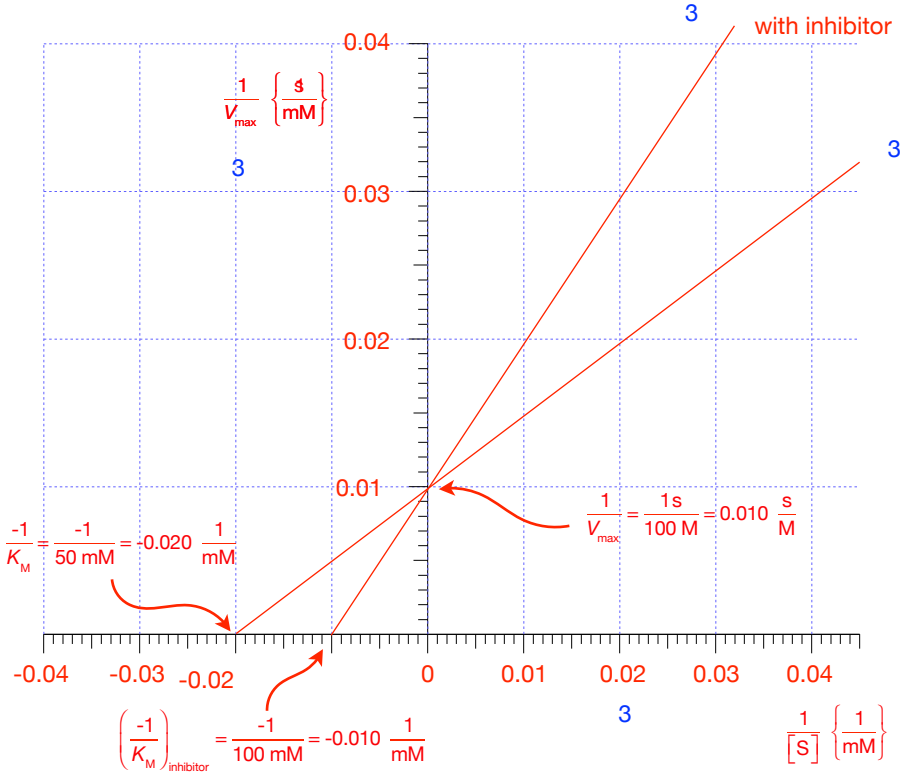
$$\frac{k_{cat}}{K_M} = \left(\frac{1.0x10^4}{mM \cdot s}\right)\left(\frac{1{,}000\ mM}{M}\right) = 1.0x10^7\ \frac{1}{M \cdot s}$$

The catalytic efficiency for *fumarase*, under the conditions examined, is an order of magnitude less than $10^8$ 1/M•s, so is not "catalytically perfect".

e. When an enzyme displays "catalytic perfection", what physical constraint has been placed on the enzyme's ability to increase rate of the reaction.

When an enzyme displays "catalytic perfection" it suggests that there are no additional modifications that can be made to the enzyme to make it more efficient. This is because further increases in the rate are no longer influenced by the enzyme, but are determined by the rate that substrate molecules can randomly diffuse into the active site of the enzyme. Under these situation we would say that the reaction is "diffusion rate-limited". 3

f. Using the axes drawn below, sketch the expected *Lineweaver-Burke Plot* for this experiment. (Be sure to label your axes, including units)




g. On the same graph, sketch the result expected in the presence of an inhibitor that increases the $K_M$ to 100 mM but has no effect on $V_{max}$.

h. Describe where the inhibitor likely binds to the enzyme, relative to the substrate.

Because the inhibitor is affecting $K_M$ and not $V_{max}$, it suggests that this is a competitive inhibitor and competes for the same binding site at the enzyme's active site as the substrate.

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3. Draw the structure of the phospholipid *phosphotidylserine* containing a stearyl (18:0) acyl group at the C1 position, and a palmitoleyl (16:1, *cis*-$\Delta^9$ ) acyl group at the C2 position.

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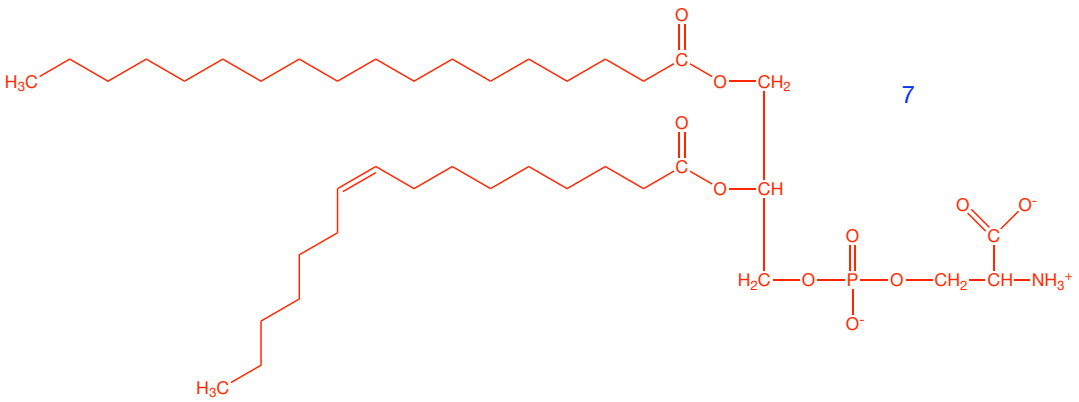

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a. In a couple of sentences, describe the structure that forms spontaneously when phosphotidylserine is mixed with water. Include in this description a mention of the intermolecular interactions that lead to the formation of this structure. Phospholipids, such as phosphotidylserine, are highly *amphipathic*, meaning they contain a moiety that is very *hydrophobic*, along with a moiety that is at the same time very *hydrophilic*. When placed in water these molecules will aggregate in away that satisfies both of these characteristics. Phospholipids form lipid bilayers, in which the surfaces of the bilayer expose the hydrophilic moieties to water, while at the same time burying the hydrophobic regions on the inside of the bilayer and away from exposure to water. Once formed, the bilayer structure is then stabilized by the favorable hydrogen bonding interactions between the exposed serine phosphate head group and the water, and the vander Waals interactions between the fatty acid acyl side chains.

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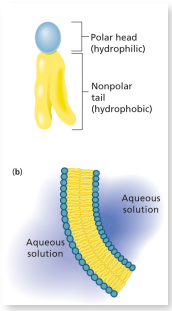


4. Below is a figure illustrating the active site of an enzyme found in the glycolytic pathway. The enzyme catalyzes the following reaction,

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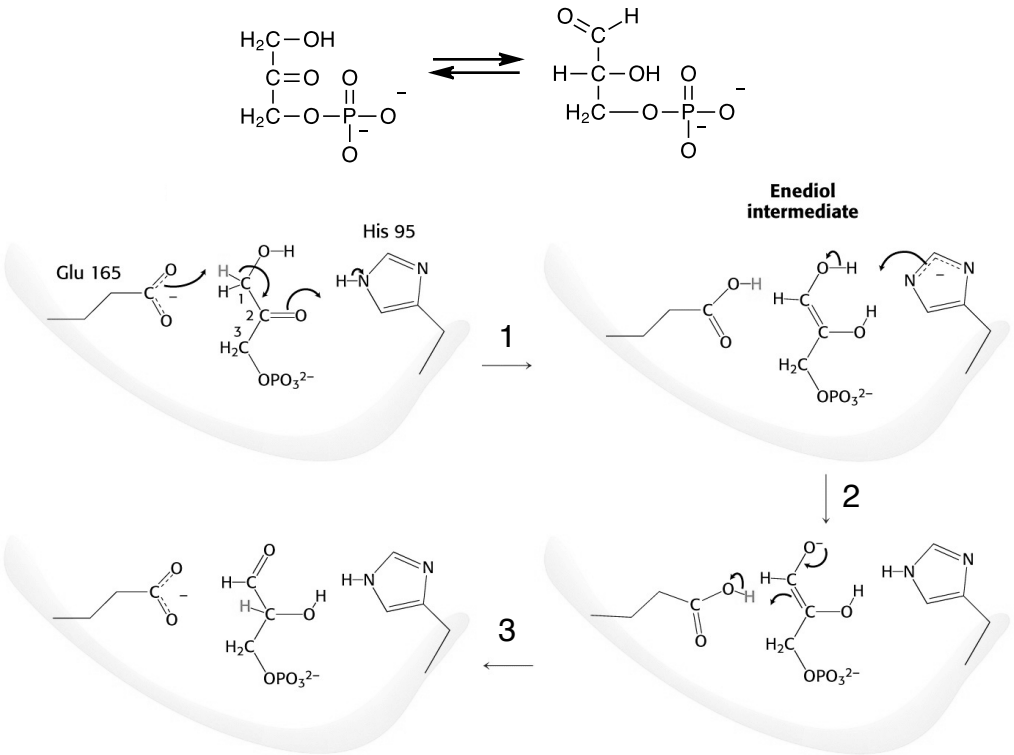

a. What class of biological molecule, *e.g.*, amino acid, carbohydrate, lipid, *etc.* does the reactant in this reaction belong to? carbohydrate (sugar phospahte) 2

b. What is the name of the product for this reaction? glyceraldehyde 3-phosphate 2

c. What class of enzyme does this enzyme belong to? 2 Isomerase

One reactant and one product, so the two must be isomers of one another.

d. What catalytic role does *His 95* play in step 2 of this reaction? 2 acid/base catalyst

e. What catalytic role does *Glu 165* play in step 3 of this reaction? 2 acid/base catalyst

5. *Amylose* and *cellulose* are both polymers of D-glucose, however their chemical and physical properties are quite distinct.

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a. In a couple of sentences, describe some of the structural and physical differences between amylose and cellulose. Also include in this discussion how these differences relate to biological roles played by these two polysaccharides. Both are linear polymers of D-glucucose, but in amylose the D-glucose monomers are connected to one another by α(1→4) glycosidic bonds, while in cellulose they are connected by β(1→4) glycosidic bonds. While a seeming small chemical difference, this leads to a marked difference in their physical properties. Amylose has a very open helical shape that becomes highly hydrated with placed in water, whereas with cellulose, the polymer strands form a dense network hydrogen bonds with other polymer strands to form a strong, insoluble fiber. These differences suites each polymer to its biological role; amylose is used in plants to store glucose for future energy needs, whereas cellulose plays a structural role in plants. Complimenting these roles is the fact that very few organisms produce the enzymes need to break down cellulose, but those needed to break down starch are widely available. 10

6. Myoglobin (Mb) and hemoglobin (Hb) are both oxygen binding proteins.

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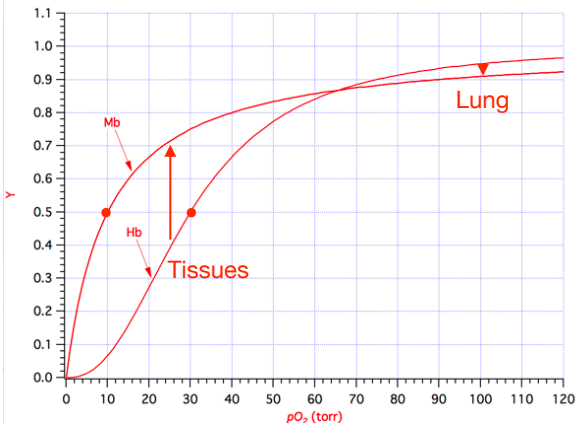
a. Though both proteins bind oxygen, they do so for different reasons. In mammals, describe the role that each protein performs when binding oxygen.

Mb: Myoglobin's role is to bind and store oxygen in the tissues until needed. It has a heme group cofactor that binds the $O_2$ and gives the protein a red color. 4

Hb: Hemoglobin's role is to bind oxygen in the lung and then transport it through the blood stream to the tissues. 4

b. On the graph to the right, sketch and label the oxygen binding curves, fraction bound (Y) *vs.* partial pressure of oxygen in *torr* ($pO_2$), for Mb with a $P_{50}$ of 10 torr and Hb with a $P_{50}$ of 30 torr. Be sure to label the axes.

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c. Given the $pO_2$ is 100 torr in the lungs and 26 torr in the tissues, explain how the differences in the binding behaviors for Mb and Hb shown in the graphs above best suites each to the roles you described in part a. When in the lung, hemoglobin will become nearly 100% saturated with oxygen, but as travels out to the tissues where the partial pressure is lower, it binding affinity for oxygen falls off more rapidly than myoglobin's. This allow it to more readily pass of the oxygen off to an awaiting myoglobin molecule. 4

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