

There are 106 possible points (6 bonus points) on this exam. There are 8 pages.

$$v_o = \frac{V_{\max} \times [S]}{K_m + [S]} \quad k_{\text{cat}} = \frac{kT}{h} e^{-\Delta G^\ddagger / RT} \quad V_{\max} = k_{\text{cat}} \times E_t \quad \Delta G'^{\circ} = -RT \ln K'_{\text{eq}}$$

$$\begin{array}{ll} \text{rate}_{\text{forward}} = k_{\text{forward}}[\text{reactants}] & K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} \\ \text{rate}_{\text{reverse}} = k_{\text{reverse}}[\text{products}] & \end{array}$$

CH ₃ COOH	K _a = 1.78 × 10 ⁻⁵	H ₂ P0 ₄ ⁻²	= 3.98 × 10 ⁻¹³
H ₃ P0 ₄	K _a = 7.25 × 10 ⁻³	H ₂ CO ₃	K _a = 1.6 × 10 ⁻⁴
H ₂ P0 ₄ ⁻	K _a = 1.38 × 10 ⁻⁷	HCO ₃ ⁻	K _a = 4.68 × 10 ⁻¹¹

For the reaction of water with carbon dioxide: $K_{\text{eq}} = 1.69 \times 10^{-3}$

Remember: at constant enzyme concentration under saturation conditions, $k_{\text{cat}} \propto V_{\max}$

$$R = 8.315 \text{ J/mole} \cdot \text{K} \quad k = 1.381 \times 10^{-23} \text{ J/K} \quad h = 6.636 \times 10^{-34} \text{ J} \cdot \text{sec}$$

1. (10 points) Chymotrypsin (Mr 21,600) degrades peptides. Under saturation conditions, the substrate glycylytyrosinylglycine(GYG), is cleaved at a rate of 2.7 moles/min, k_{cat} is 100 sec⁻¹, and K_m is 108 mM. The rate of the uncatalyzed reaction is 2.7 μmoles/min. Show your work.

a. What is the enzyme concentration?

b. What substrate concentration will give a velocity that is 1/4 of V_{\max} ?

c. What is the difference between the activation energy for the reaction catalyzed by chymotrypsin and the activation energy for the uncatalyzed reaction? Calculate the value that the activation energy is changed by the enzyme.

d. What are the products of this reaction?

Each Multiple Choice Question (13) is worth 2 points, circle the best answer on this exam:

2. Why do plants and animals store “quick” energy as high molecular weight branched polymers.
- I. To maximize the number of free reducing ends
 - II. To decrease entropy
 - III. To increase osmotic pressure
 - IV. To increase the rate of the hydrolysis reaction by increasing the substrate concentration

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

3. A simple plot of V_0 versus $[S]$ is superior to a double-reciprocal plot ($1/V_0$ versus $1/[S]$) for:

- A. determining V_{max} .
- B. determining the type of inhibition.
- C. determining the K_m .
- D. detecting allosteric regulation.
- E. none of these

4. In competitive inhibition, increasing concentrations of the inhibitor will have the following effect on the kinetics of the enzyme:

- A. V_{max} will stay the same.
- B. K_m will decrease.
- C. The reaction will cease because the inhibitor binds irreversibly.
- D. K_m / V_{max} will stay the same.
- E. None of these, or more than one of these, circle all correct answers

5. Which of the following is **true** about zymogens?

- A. Zymogens cleave proteases.
- B. Zymogens are inactivated by inhibitor proteins.
- C. Proproteins are one type of zymogen.
- D. Zymogens are enzymatically inactive.
- E. None of these or more than one of these, circle all true statements

6. Which of the following is **not true** about the phosphorylation of proteins?

- A. Proteins are usually phosphorylated at Ser, Thr or Tyr amino acids.
- B. Dephosphorylation of proteins is catalyzed by phosphatases.
- C. Phosphorylation always activates enzymes.
- D. Glycogen synthase is regulated by multiple phosphorylations.
- E. None of these

7. Which of the following is **true** about the role of enzymes in catalyzing chemical reactions?

- A. Enzymes eliminate the activation energy of a reaction.
- B. Enzymes are only needed if the reaction has a K_{eq} that is less than one.
- C. Enzymes enhance the rate of forward and reverse reactions.
- D. Enzymes alter the equilibrium of a reaction to favor products.
- E. None of these.

8. Which of the following is **true** about specific acid-base catalysis?

- A. It requires the ions of water.
- B. Amino acid side chains on enzymes can act as proton donors or acceptors.
- C. Often involves covalent bonds formed between a metal ion and the substrate.
- D. It involves a transient covalent bond between the enzyme and the substrate
- E. none of these.

9. The steady state of an enzyme-catalyzed reaction is reached when
- A. the rate of enzyme-substrate formation is constant.
 - B. the concentration of enzyme-substrate complex equals the concentration of product.
 - C. the rate of disappearance of reactant is constant.
 - D. the concentration of the enzyme-substrate complex is constant over time.
 - E. none of these

10. An enzyme-catalyzed reaction was carried out with the substrate concentration initially a thousand times greater than the K_m for that substrate. After 9 minutes, 1% of the substrate had been converted to product, and the amount of product formed in the reaction mixture was 12 mmol. If, in a separate experiment, one-third as much enzyme and twice as much substrate had been combined, how long would it take for the same amount (12 mmol) of product to be formed?
- A. 1.5 min
 - B. 13.5 min
 - C. 27 min
 - D. 3 min
 - E. 6 min
- F. None of these, the correct answer is _____

11. The reducing end of a disaccharide or a polysaccharide is
- A. the end with an anomeric carbon that cannot be oxidized.
 - B. the end that does not have an anomeric carbon.
 - C. the end of a chain with a free anomeric carbon (i.e., not involved in a glycosidic bond).
 - D. The end whose sugar cannot take the linear form
 - E. None of these

12. Why is glucose not stored in its monomeric form in cells?
- I. Because monomeric glucose would raise the osmolarity of the cytosol to unsafe levels.
 - II. Because the monomeric form of glucose is not very soluble.
 - III. Because the monomeric form of glucose has a free reducing end.
 - IV. Because glucose monomers spontaneously form polymers in the cell.
- a. I and III b. II and IV c. I, II and III d. IV only e. none of these

13. In starch and glycogen, the glucose monomers are joined by ($\alpha 1 \rightarrow 4$) linkages, whereas in cellulose, the glucose monomers are joined by ($\beta 1 \rightarrow 4$) linkages. What is a biological consequence of this difference in sugar linkage?
- I. Cellulose is generally not digestible by animals, whereas starch is easily digestible.
 - II. Starch takes on a helical structure and cellulose forms fibers.
 - III. Glycogen is water soluble and cellulose has more tensile strength.
 - IV. Glycogen is unbranched, while cellulose is highly branched.
- a. I and III b. II and IV c. I, II and III d. IV only e. none of these

14. Lectins are
- A. carbohydrates that can bind a protein with high specificity.
 - B. proteins linked to carbohydrates.
 - C. the oligosaccharide moieties on glycoproteins.
 - D. proteins that bind carbohydrates with high specificity.
 - E. None of these

15. (8 points) When glucagon binds to its receptor on a liver cell, a chain of events occurs that

ultimately increases blood glucose levels. Describe this chain of events.

16. (6 points) Draw the three possible structures for D-galactose. Label them as D-galactose, α -D-galactose, and β -D-galactose. Draw an arrow to the anomeric carbon(s).

17. (8 points) Give the best answer for the following questions:

- A) Proteins that “read the sugar code” bind to specific oligosaccharides, what are these proteins called?
- B) What type of molecule is responsible for the A,B,O blood groups?
- C) A newer test that measures a patient’s regulation of blood glucose detects a protein that reacts with glucose. What is the name of this glucose-protein adduct?
- D) Give an example of a heteropolymer of glucose derivatives that provides structural support in cartilage.
- E) What specific molecule is on the outside of endothelial cells and binds to oligosaccharides on leukocytes to slow them down in the blood flow?
- F) What heteropolymer of glucose derivatives is the mostly highly negatively charged biomolecule is present in the extracellular network and provides a binding site for antithrombin and thrombin?
- G) What very large heteropolymer of glucose is found in the vitreous humor of the eyeball?
- H) What heteropolymer of glucose is found in the cornea, bone and cartilage and is often aggregated with chondroitin sulfate?

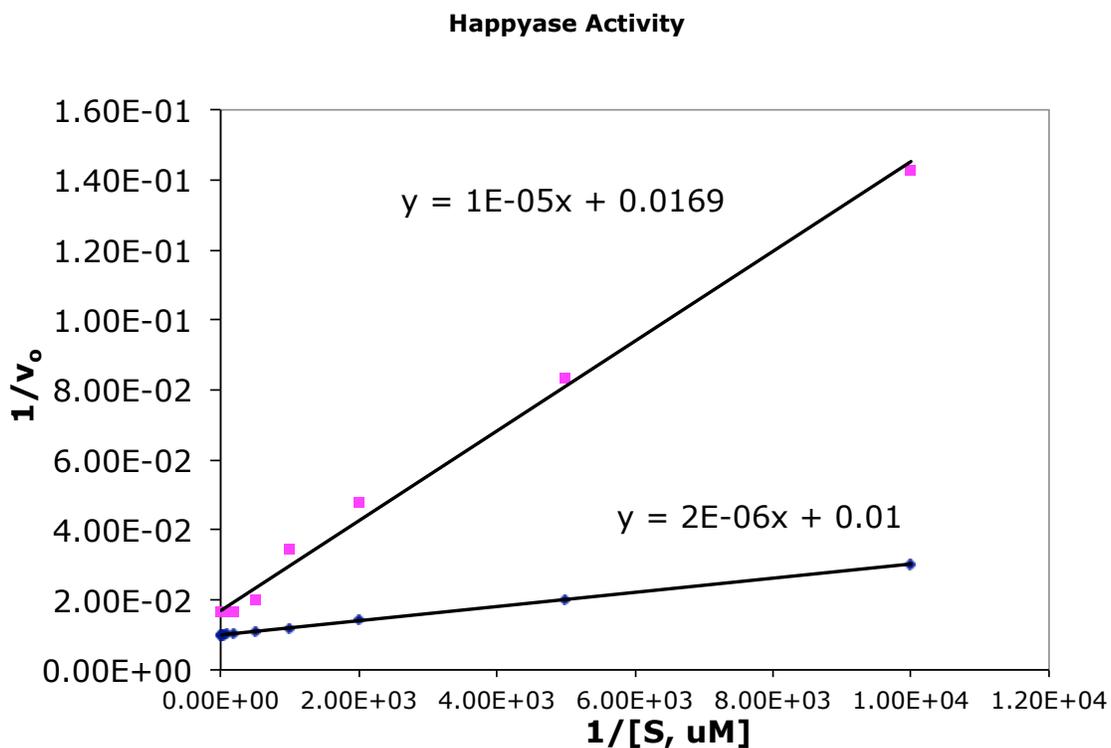
18. (6 points) Briefly describe the structure and function of the following:

A) Glycogen

B) Chitin

20. (20 points) Using complete sentences and structures, describe the enzyme mechanism that your group presented during the parade of mechanisms. Be sure to include the types of catalysis that are involved. Be specific and give details.

21. (12 points) Happyase is a naturally occurring enzyme that reacts with sugar to form molecules that act like the active ingredient in chocolate. With Happyase, all is grand. However, Happyase is inhibited by a compound called Nosleepite. An experiment was done to measure the effect of Nosleepite on Happyase and the data is shown in the following graph. (You need to determine which line is for the experiment with Nosleepite.) The velocity of the reaction is measured in mmol/sec, the concentrations of the substrate (Sugar) were micro Molar.



Complete the following table

Experiment	K_m	V_{max}
Happyase		
Nosleepite + Happyase		

What type of inhibition is this?

Does Nosleepite bind to Happyase or to Happyase-Sugar or to either Happyase or Happyase-Sugar?