CHEM 4400 Exam 3 Fall 2012 Dr. Stone Name_____

$$V_0 = \frac{V_{max} \times [S]}{K_m + [S]} \qquad k_{cat} = \frac{kT}{h} \times e^{\frac{-G^{\ddagger}}{RT}} \qquad V_{max} = k_{cat} \times E_t \qquad \Delta G^{\circ\prime} = -RT \ln K'_{eq}$$

$rate_{forward} = k_{forward}[reactants]$ $K_{eq} = \frac{[products]}{[reactants]}$ CH_3COOH Ka = 1.78×10^{-5} $H_2PO_4^{-2} = 3.98 \times 10^{-13}$

$rate_{reverse} = k_{reverse}[products]$ H_3PO_4 Ka = 7.25×10^{-3} H_2CO_3 Ka = 1.6×10^{-4}

$H_2PO_4^-$ Ka = 1.38×10^{-7} HCO_3^- Ka = 4.68×10^{-11}

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

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

R = 8.315 J/mole*K k = 1.381×10^{-23} J/K h= 6.636×10^{-34} J*sec.

1. (6 points) Draw the three possible structures for D-glucose. Label them as D-glucose, α-D-glucose, or β-D-glucose.

2. (10 points) Put the letter of **one** of the following choices by the descriptions below. Answers could be used more than once, some may not get used.

a. Chitin
b. Sucrose
c. Cellobiose
d. Chondroitin
e. Lectin
f. Cellulose
g. Lactose
h. Hemoglobin glycation product
i. trehalose
j. Advanced glycation end products
k. Maltose
l. Keratan
m. hyaluronate

_____Disaccharide of galactose and glucose monomers with β(1→4) linkages

_____ Circulating form of energy in insects.

_____Circulating form of energy in plants

_____A glucosmaminoglycan found in the vitreous humor (the glassy part of the eyeball)

_____A glucoseaminoglycan found in skin, hair and nails

_____Heteropolymer of glucose with a β(1→4) linkage, provides support in cartilage

_____ Proteins that bind to specific oligosaccharides

_____Used to determine circulating blood glucose levels over a period of weeks

_____Disaccharide of glucose with α(1 → 4) linkages

_____Disachharide of glucose that does not have a free anomeric carbon

3. (5 points) Glucose is a form of circulating energy in mammals. Why are levels of glucose closely regulated? (High levels are toxic—why?)

4. (3 points) Which of following is an anomeric pair?

A) β–D-glucose and β–D-mannose
B) α-D-fructose and β-D-fructose
C) β–D-glucose and β–L-glucose
D) α–D-galactose and α–L-fructose
E) α-D-fructose and β-L-fructose.

5. (10 points) Briefly describe the type of regulation that is used to control the activity of each of the following enzymes:

a. Glycogen phosphorylase

b. cAMP dependent protein kinase

c. Phosphorylase kinase

d. Trypsin

e. phosphoprotein phosphatase

6. (6 points) Compare and contrast glycogen and cellulose. They have different linkages and structures and functions. Relate the linkages to the structures and the structures to the functions.

7. (3 points) The steady state of an enzyme-catalyzed reaction is reached when

A.) the rate of appearance of product over time is constant.
B.) the rate of enzyme-substrate formation is constant.
C.) the concentration of enzyme-substrate complex equals the concentration of product.
D.) the concentration of the enzyme-substrate complex is constant over time.
E.) None of these

8. (3 points) A good transition-state analog:
A) binds covalently to the enzyme.
B) binds to the enzyme more tightly than the substrate.
C) binds very weakly to the enzyme.
D) is too unstable to isolate.
E) must be almost identical to the substrate

9. (5 points) An enzyme-catalyzed reaction was carried out with the substrate concentration initially a thousand times greater than the K_m for that substrate. After 12 minutes, 1% of the substrate had been converted to product, and the amount of product formed in the reaction mixture was 24 μmol. If, in a separate experiment, one third (1/3) as much enzyme and twice as much substrate had been combined, how long would it take for the same amount (24 μmol) of product to be formed? (Show your reasoning.)

10. (10 points) Happyase is a naturally occurring enzyme that synthesizes 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 date is shown in the following graph. (You need to determine which line is for the experiment with Nosleepite.) The initial velocities have units of sec^{-1} and the substrate concentrations were μM.

11
12

a. What is the Vmax for the uninhibited enzyme? Show your work.

b. What is the Km for the inhibited enzyme? Show your work.

c. What type of inhibition is this? How are you able to determine this?

d. Does the nosleepite bind to the enzyme, the enzyme substrate complex or to either the enzyme or the enzyme substrate complex?

11. (3 points) Which of the following is true about zymogens?
    A.) Proproteins are one type of zymogen.
    B.) Zymogens are inactivated by inhibitor proteins.
    C.) Zymogens are enzymatically inactive.
    D.) Zymogens cleave proteases.
    E.) Chymotrypsin is regulated by binding to a zymogen

12. (10 points) Using complete sentences and structures, describe the types of catalysis that are involved in the enzyme mechanism that your group presented during the parade of mechanisms. Be specific and give details.

13. (12 points) Chymotrypsin (Mr 21,600) degrades peptides by cleaving the amide bond on the carboxyl side of aromatic amino acids. The following amino acids play important roles in the mechanism of catalysis: G_{193}, S_{195}, H_{57}, A_{102}. Under saturation conditions, the substrate glycyltyrosinylglycine, is cleaved at a rate of 4.1 moles/min, kcat is 100 sec^{-1}, and Km is 90 mM. The rate of the uncatalyzed reaction is 65 nmoles/min. The temperature is 37°C.

a. What is the catalytic triad?

b. What amino acid is involved in covalent catalysis?

c. What amino acid is involved in general acid and general base catalysis?

d. What is role of the hydrophobic pocket?

e. What is the role of the oxyanion hole? What amino acids form the oxyanion hole?

f. What is the difference in activation energy for the catalyzed vs uncatalyzed reaction. (Show all of your work.)

14. (14 points) For the parade of mechanisms, complete the following table for the mechanisms that were presented in class:

Name of enzyme	Substrate	Product	Brief description
