C383 Exam 2 Version 1
Spring 2017

Name Key Seat Number _____

Student ID _____ Circle your section: **Fidel: M R**
Goran: W R

The last page of this exam contains equations, constants, and area for scratchwork.

The exam consists of 35 questions worth 110 points on a total of ____ pages. It will be scored out of 100 points, with the maximum score being 100.

1-15 _____/30 multiple choice

16-30 _____/30 fill in the blank

31 _____/10

32 _____/10

33. _____/10

34. _____/10

35. _____/10

Total:

Regrading: All requests for regrades must be submitted in writing within 48 hours of the return of the exam. You must explicitly state what has been misgraded and why it is an error. The entire exam will be regraded, which could result in points being added or deducted overall.

Section 1: Multiple Choice. 15 questions, 2 points each.

1. For an enzyme reaction that follows Michaelis-Menten kinetics, when concentrations of substrate are low, the reaction is

A. first order with respect to substrate
B. first order with respect to enzyme
C. zero order with respect to substrate
D. zero order with respect to enzyme
E. Both A and B
F. Both A and D

2. If you know the maximum velocity of an enzyme mediated reaction, you can determine the turnover number if you know

A. the concentration of enzyme
B. the specificity constant
C. k_{cat}
D. K_M
E. none of the above

3. If an enzyme is placed in a lower than optimal pH, its loss of activity might be due to

A. an active site general acid being protonated
B. an active site general base being protonated
C. an active site general acid being deprotonated
D. an active site general base being deprotonated
E. none of the above

4. An uncompetitive inhibitor

A. is relatively most effective at high substrate concentrations
B. binds only to the enzyme substrate complex
C. raises the value of K_M
D. Raises the value of V_{max}
E. more than one of the above

5. Which of these amino acids is most least likely to be involved in covalent catalysis in an enzyme active site?

A. Phenylalanine
B. Serine
C. Threonine
D. Lysine
E. Cysteine

6. Which of these statements does not apply to both myoglobin and hemoglobin?

A. requires a "distal histidine" for oxygen binding
B. oxygen binding is affected by change in pH
C. binds a heme group
D. hydrophobic pocket protects oxidation of iron ion
E. nearly saturated with oxygen at high oxygen partial pressure

7. How do starch and cellulose differ?

A. They are epimers.
B. They are composed of different monosaccharides.
C. One is a polysaccharide and the other is a oligosaccharide.
D. They have different orientation around their glycosidic bond.

8. _____ is the process by which a compound can cross a membrane through a transporter into a region of lower concentration.

A. Active transport
B. Secondary transport
C. Active diffusion
D. Facilitated diffusion

9. The sodium/potassium transporter can be described in all of these ways except:

A. antiporter
B. P-type ATPase
C. Active transporter
D. ABC transporter

10. The most common mutation in Ras that leads to human cancers

A. causes a key second messenger not to be produced.
B. inactivates a kinase.
C. disrupts GTPase activity.
D. blocks Ca^{+2} influx.
E. disrupts ligand/receptor binding.

11. Which of the following digestive enzymes would break an ester bond?

A. lipase
B. protease
C. peptidase
D. amylase
E. lactase

12. Digestion of which of the following dietary components requires release of bile salts into the intestine?

A. proteins
B. vitamins
C. tiracylglycerides
D. polysaccharides
E. disaccharides

13. _____ is the activated carrier of two-carbon fragments.

A. NADH
B. Coenzyme A
C. Coenzyme Q
D. FAD
E. ATP

14. Under which of these circumstances is the reaction R → P always spontaneous?

A. a reaction with $+\Delta G^{O'}$ and [P] > [R]
B. a reaction with $-\Delta G^{O'}$ and [P] > [R]
C. a reaction with $+\Delta G^{O'}$ and [P] < [R]
D. a reaction with $-\Delta G^{O'}$ and [P] < [R]
E. More than one of the above

15. Which of the following molecules is most oxidized?

A. methanol
B. methanoic acid (formic acid)
C. methane
D. methaldehyde (formaldehyde)

Section 2: Fill in the blank. 15 questions 2 points each

16. An enzyme has reached catalytic perfection when k_{cat}/K_m approaches the diffusion limit.

17. A noncompetitive enzyme inhibitor lowers the apparent V_{max} of an enzyme and is able to bind to the free enzyme.

18. Allosteric enzymes have active sites and distinct regulatory sites that allow for cooperativity and make their kinetics more complicated than Michaelis-Menten.

19. When glycerol is condensed with three fatty acids, it is called a triacylglyceride.

20. Glycolipids are cell membrane components that have carbohydrate residues attached to a diacylglyceride tail.

21. Draw a (18:2) cis-$\Delta^{9,12}$ fatty acid:

22. The thermodynamic driving force for formation of the lipid bilayer is hydrophobic effect.

23. A membrane channel that only opens when there is a change in membrane potential (charge across the membrane) is called a voltage-gated transporter.

24. cAMP and IP_3 are examples of second messengers in signaling pathways.

25. Two major classes of signal transduction receptors are GPCR and receptor tyrosine kinases.

26. cAMP produced through the β-adrenergic receptor pathway binds to the regulatory subunit of the enzyme PKA, which activates and inactivates enzymes through phosphorylation.

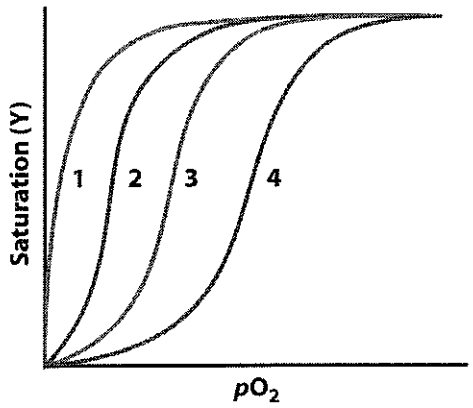
27. Attachment of chemical groups to an enzyme to change its activity (most often phosphorylation and dephosphorylation) is a regulatory strategy called covalent modification.

28. All of the digestive enzymes belong to the enzyme class hydrolase, but work on different substrates.

29. Omeprazole (Prilosec) treats acid reflux by inactivating the H^+/K^+ pump.

30. One measure of the energy status of a cell is called the energy charge, which is defined as the fraction of adenosine nucleotides in the form of ATP relative to the total concentration of ATP, ADP, and AMP.

31. (10pts) Below is a figure with several oxygen dissociation curves. Assume that curve 3 corresponds to hemoglobin with physiological concentrations of carbon dioxide and 2,3-BPG at pH 7. Which curve represent each of the following perturbations? Give a SHORT explanation for each.



Problem 9.18
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+2 each

A. Hyperventilation leads to decrease in CO_2 levels

2: Shift toward R state of allosteric protein or (other answers possible) increase in binding affinity

B. Increase in 2,3BPG

4: shift toward T state of allosteric protein decrease affinity, etc

C. Increase in pH

2: shift toward R state increase affinity, etc

D. Mutation that leads to loss in quaternary structure

1: No longer cooperative

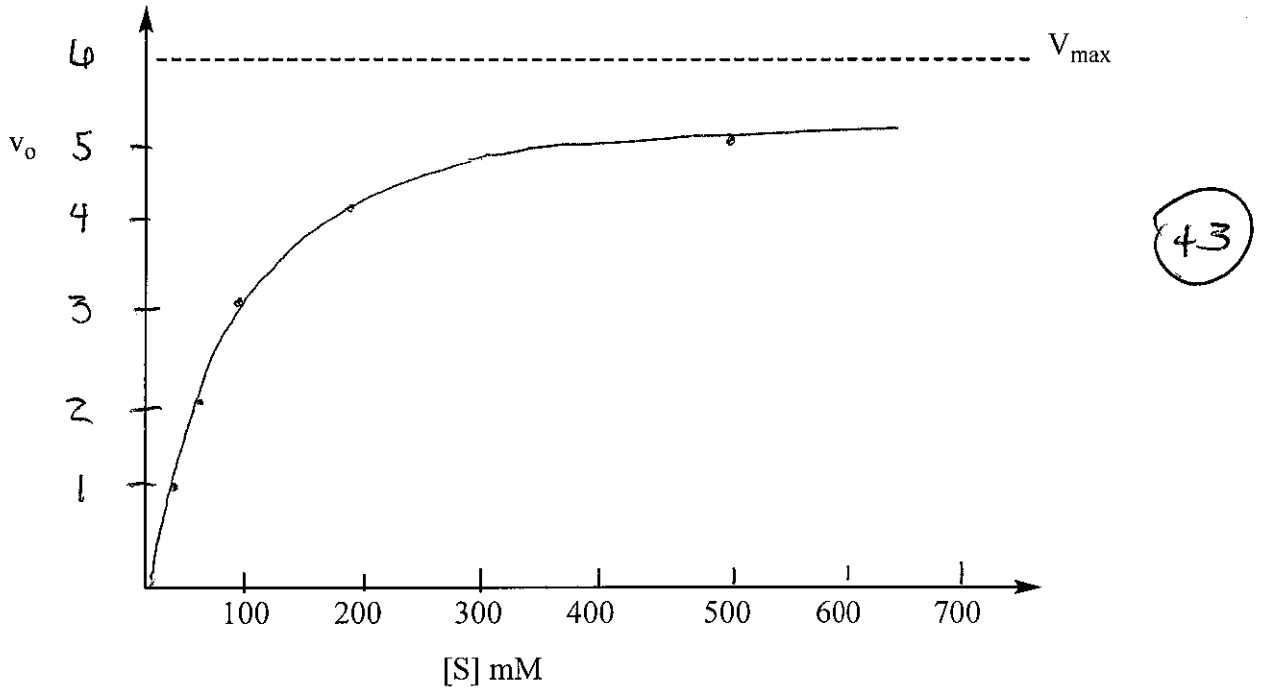
E. Mutation which stabilizes the central cavity and favors tense conformation

4: Decrease in binding affinity, etc

32. You are investigating a new enzyme through Michaelis Menten kinetics, and you have found that it has a maximum velocity of 6.0 μM/s when the [E] is 1.5×10^{-9} M based on the following data:

Initial velocity	[S]
1.0 μM/s	20 mM
2.0 μM/s	50 mM
3.0 μM/s	100 mM
4.0 μM/s	200 mM
5.0 μM/s	500 mM

A. Draw a Michaelis Menton graph to scale on the graph below:



+3

B. What is K_M for this enzyme? How did you determine this value?

+4

$K_m = 100\ mM$ - it is the [S] at which $V_o = \frac{1}{2} V_{max}$

C. Calculate the specificity constant (k_{cat}/K_M) for this enzyme. (Show all work.)

+3

$V_{max} = k_{cat}[E]$

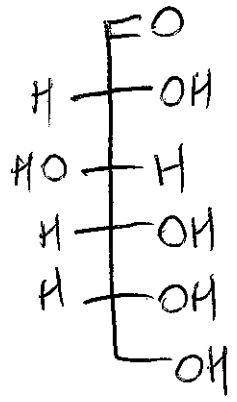
$k_{cat} = \frac{6 \times 10^{-6}\ M/s}{1.5 \times 10^{-9}\ M} = 4000\ s^{-1}$

$\frac{k_{cat}}{K_m} = \frac{4000}{0.1\ M} = 4.0 \times 10^4\ M^{-1} s^{-1}$

33. (10pts) Draw each of the following carbohydrates:

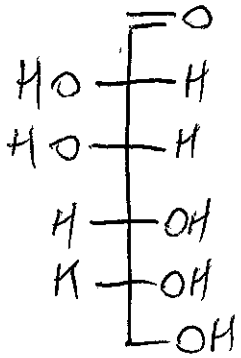
straight chain form of D-glucose

+2

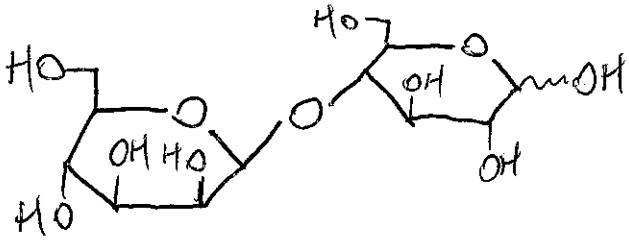


straight chain form of D-mannose

+2



dissaccharide of D-glucose and D-mannose with β(1→4) glycosidic bond with mannose on the nonreducing end



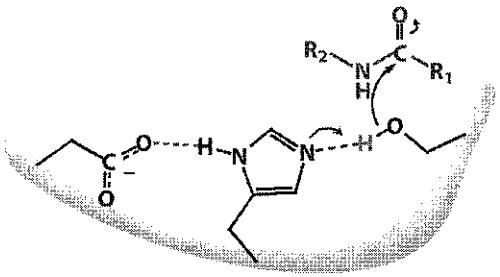
mannose reducing +1

β +1

1→4 +2

+2 no stereochem mistakes based on above

34. (10pts) Answer the following questions based on the catalytic mechanism of chymotrypsin. Its catalytic triad and substrate are shown below:



What is the role of histidine in this mechanism?

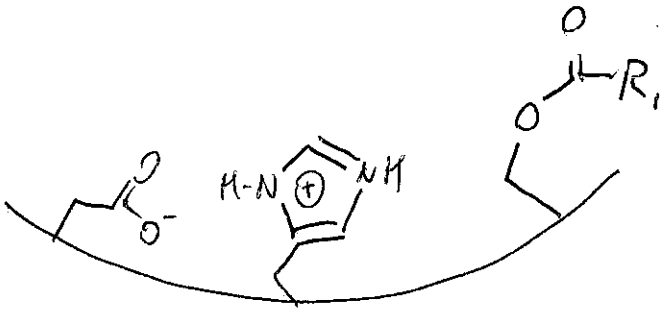
+2 General base to deprotonate serine

What is the role of serine in this mechanism?

+2 Nucleophile in nucleophilic catalysis to help break

Half way through the reaction, an acyl-enzyme intermediate forms. Draw it below, based on the figure above.

+3



Why would the catalytic ability of the enzyme be effected if aspartate were mutated to alanine?

+3 Decreased because histidine would not be as reactive of a base - not effective in activating serine for Nu: catalysis.

35. (10pts) Calculate the standard free energy for the transfer of a phosphate from glucose-6-phosphate to glycerol-3-phosphate.

Glucose-6-P + glycerol → Glucose + glycerol-3-P

G-6-P → Glc + Ⓟ $\Delta G^{o'} = -13.8 \frac{KJ}{mol}$

glycerol + Ⓟ → G-3P $\Delta G^{o'} = 9.2 \frac{KJ}{mol}$

$\Delta G^{o'} = -4.6 \frac{KJ}{mol}$

+5

This reaction does not happen in typical cells, so you are trying to design an enzyme to catalyze the reaction. You have tested your new enzyme, and it seems to work, but when you test it in a cell with [glucose] = 4 mM, [glucose-6-P] = 1.0 mM, [glycerol] = 0.1 mM, and [glycerol-3-P] = 0.16 mM at 298K, the concentrations of the reactants and products do not change. Explain.

$$\Delta G' = \Delta G^{o'} + RT \ln \frac{P}{R}$$

$$= -4600 \frac{J}{mol} + 8.314 \frac{J}{mol\,K} (298) \ln \frac{[.00016][.004]}{[0.001][0.0001]}$$

$\Delta G' =$ zero

+5

* Under these conditions, the concentrations are already at equilibrium, so the enzyme will not change the concentrations.

Useful Information:

$$\Delta G_{reaction} = \Delta G^{\circ\prime}_{reaction} + RT \ln \frac{[products]}{[reactants]}$$

$\Delta G^{0'} = -RT \ln K_{eq}$ $\quad R = 8.314$ J/mol.K

$V_o = V_{max}[S]/(K_M + [S])$

TABLE 12-4

Standard Free Energy Change for Phosphate Hydrolysis

Compound	$\Delta G^{\circ\prime}$ (kJ · mol^{-1})
Phosphoenolpyruvate	−61.9
1,3-Bisphosphoglycerate	−49.4
ATP $\longrightarrow$ AMP + PP_i	−45.6
Phosphocreatine	−43.1
ATP $\longrightarrow$ ADP + P_i	−30.5
Glucose-1-phosphate	−20.9
$PP_i \longrightarrow 2\,P_i$	−19.2
Glucose-6-phosphate	−13.8
Glycerol-3-phosphate	−9.2

Area for scratch work: (Nothing on this page will be graded.)