Name Key

Biochemistry 5700
Fall 2010
Final Exam
December 15, 2010

INSTRUCTIONS:

Do not begin until 9:30 AM. The exam must be turned in by 11:20 AM. This exam contains two sections: the "new material" section and the "comprehensive" section. There are 70 total questions (35 new material, 35 comprehensive).
Answer the questions by marking on the scantron sheet using a #2 pencil. Turn in the scantron when you are finished. Good Luck!!

Equations: $\Delta G = \Delta G^{\circ\prime} + RT\ln Q$ $\quad \Delta E = \Delta E^{\circ\prime} - \frac{RT}{nF}\ln Q$ $\quad \Delta G' = -nFE'$

$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[A^-]}{[HA]}$ $\quad v = \frac{V_{max}\cdot[S]}{K_m + [S]}$

Constants: F = 96.5 kJ/V•mol R = 8.3144 J/mol•K

table 5-1

Properties and Conventions Associated with the Standard Amino Acids

Amino acid	Abbreviated names	M_r	pK_a values: pK_1 (—COOH)	pK_2 ($—NH_3^+$)	pK_R (R group)
Glycine		75	2.34	9.60	
Alanine		89	2.34	9.69	
Valine		117	2.32	9.62	
Leucine		131	2.36	9.60	
Isoleucine		131	2.36	9.68	
Methionine		149	2.28	9.21	
Phenylalanine		165	1.83	9.13	
Tyrosine		181	2.20	9.11	10.07
Tryptophan		204	2.38	9.39	
Serine		105	2.21	9.15	
Proline		115	1.99	10.96	
Threonine		119	2.11	9.62	
Cysteine		121	1.96	10.28	8.18
Asparagine		132	2.02	8.80	
Glutamine		146	2.17	9.13	
Lysine		146	2.18	8.95	10.53
Histidine		155	1.82	9.17	6.00
Arginine		174	2.17	9.04	12.48
Aspartate		133	1.88	9.60	3.65
Glutamate		147	2.19	9.67	4.25

TABLE 13–7 Standard Reduction Potentials of Some Biologically Important Half-Reactions, at pH 7.0 and 25 °C (298 K)

Half-reaction	*E′° (V)*
$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$	0.816
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771
$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$	0.421
Cytochrome *f* (Fe^{3+}) + e^- ⟶ cytochrome *f* (Fe^{2+})	0.365
$Fe(CN)_6^{3-}$ (ferricyanide) + e^- ⟶ $Fe(CN)_6^{4-}$	0.36
Cytochrome a_3 (Fe^{3+}) + e^- ⟶ cytochrome a_3 (Fe^{2+})	0.35
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.295
Cytochrome *a* (Fe^{3+}) + e^- ⟶ cytochrome *a* (Fe^{2+})	0.29
Cytochrome *c* (Fe^{3+}) + e^- ⟶ cytochrome *c* (Fe^{2+})	0.254
Cytochrome c_1 (Fe^{3+}) + e^- ⟶ cytochrome c_1 (Fe^{2+})	0.22
Cytochrome *b* (Fe^{3+}) + e^- ⟶ cytochrome *b* (Fe^{2+})	0.077
Ubiquinone + $2H^+$ + $2e^-$ ⟶ ubiquinol	0.045
Fumarate^{2-} + $2H^+$ + $2e^-$ ⟶ succinate^{2-}	0.031
$2H^+ + 2e^- \longrightarrow H_2$ (at standard conditions, pH 0)	0.000
Crotonyl-CoA + $2H^+$ + $2e^-$ ⟶ butyryl-CoA	−0.015
Oxaloacetate^{2-} + $2H^+$ + $2e^-$ ⟶ malate^{2-}	−0.166
Pyruvate$^-$ + $2H^+$ + $2e^-$ ⟶ lactate$^-$	−0.185
Acetaldehyde + $2H^+$ + $2e^-$ ⟶ ethanol	−0.197
FAD + $2H^+$ + $2e^-$ ⟶ $FADH_2$	−0.219*
Glutathione + $2H^+$ + $2e^-$ ⟶ 2 reduced glutathione	−0.23
$S + 2H^+ + 2e^- \longrightarrow H_2S$	−0.243
Lipoic acid + $2H^+$ + $2e^-$ ⟶ dihydrolipoic acid	−0.29
NAD^+ + H^+ + $2e^-$ ⟶ NADH	−0.320
$NADP^+$ + H^+ + $2e^-$ ⟶ NADPH	−0.324
Acetoacetate + $2H^+$ + $2e^-$ ⟶ β-hydroxybutyrate	−0.346
α-Ketoglutarate + CO_2 + $2H^+$ + $2e^-$ ⟶ isocitrate	−0.38
$2H^+ + 2e^- \longrightarrow H_2$ (at pH 7)	−0.414
Ferredoxin (Fe^{3+}) + e^- ⟶ ferredoxin (Fe^{2+})	−0.432

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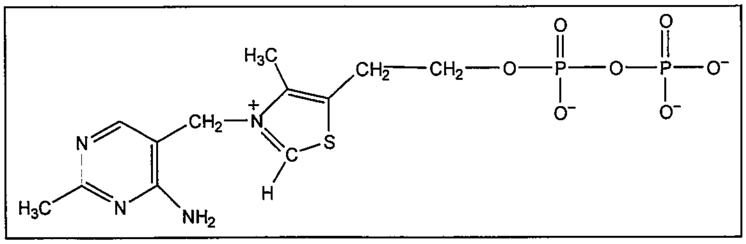

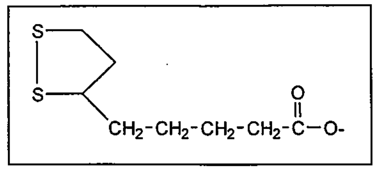

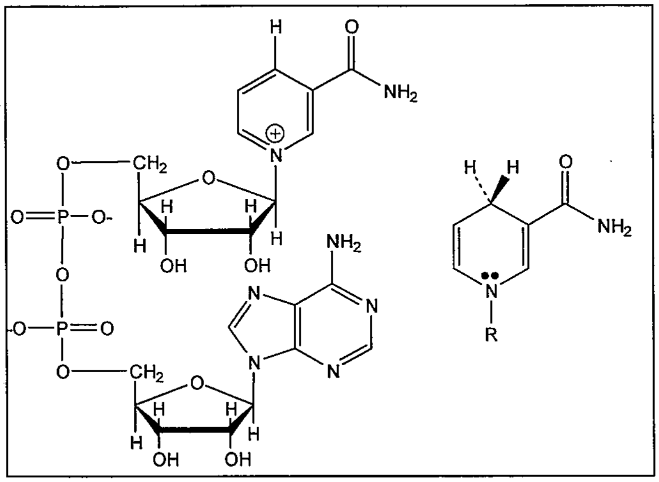

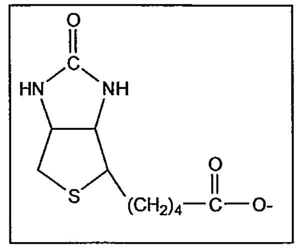

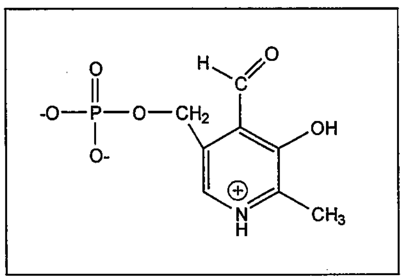

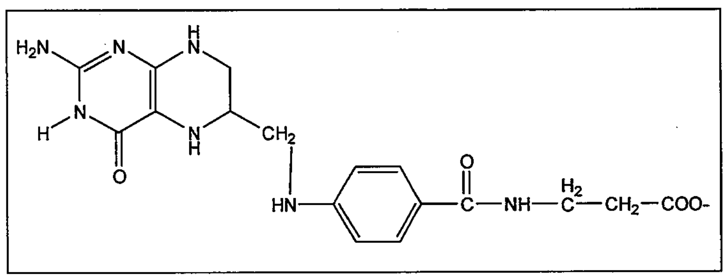

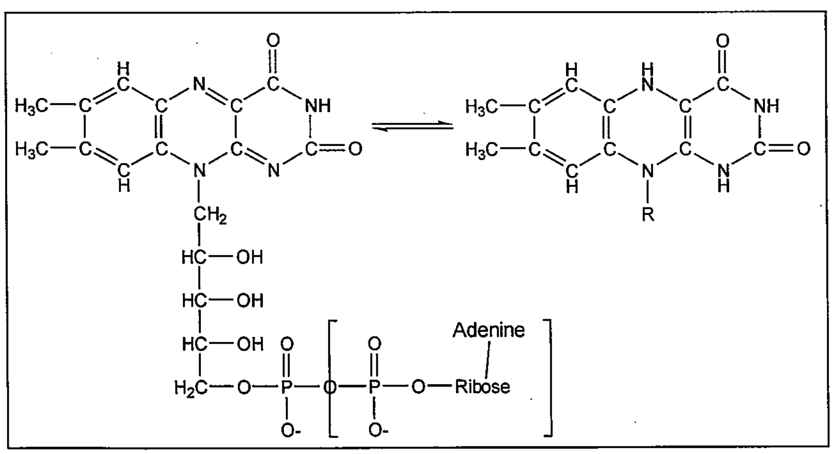

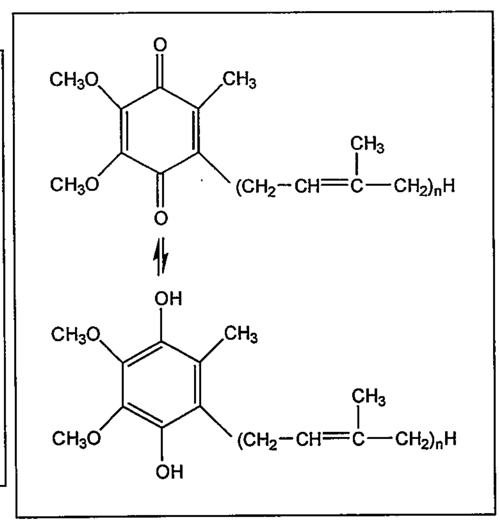

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1. Correctly order the following sequence of reactions involved in the processing of dietary fat, from first to last.

i. resynthesis of triacylglycerols from glycerol and free fatty acids = 4
ii. transport of fatty acids into intestinal epithelial cells = 3
iii. emulsification by bile salts = 1
iv. hydrolysis by intestinal lipases = 2
v. packaging of triacylglycerols in chylomicrons = 5
vi. transport of fatty acids in to myocytes or adipocytes = 7
vii. hydrolysis of triacylglycerols by lipoprotein lipase = 6

a. iii , iv , i , ii , v , vii , vi
b. iii , v , iv , i , ii , vii , vi
c. iv, iii , i , ii , v , vii , vi
d. iii , iv , ii , i , v , vii , vi
e. iii , v , vii , ii , i , iv , vi

iii, iv, ii, i, v, vii, vi

2. The regulatory cascade leading to fat breakdown in adipocytes follows what correct sequence of events?

a. hormone-receptor binding, G protein activation, adenylate cyclase activation, cyclic AMP production, lipase activation, protein kinase activation
b. hormone-receptor binding, G protein activation, adenylate cyclase activation, cyclic AMP production, protein kinase activation, lipase activation
c. hormone-receptor binding, protein kinase activation, G protein activation, adenylate cyclase activation, cyclic AMP production, lipase activation
d. hormone-receptor binding, adenylate cyclase activation, cyclic AMP production, G protein activation, protein kinase activation, lipase activation
e. hormone-receptor binding, G protein activation, cyclic AMP production, adenylate cyclase activation, protein kinase activation, lipase activation

3. What is the correct sequence of events by which fatty acids are transported and processed from the cytosol to the mitochondrion? FA-AMP FACoA - FA carnitine - FACoA

a. fatty acid, fatty acyl-CoA, fatty acyl-AMP, fatty acyl-CoA, fatty acyl carnitine
b. fatty acid, fatty acyl-phosphate, fatty acyl carnitine, fatty acyl-CoA
c. fatty acid, fatty acyl-CoA, fatty acyl-AMP, fatty acyl carnitine, fatty acyl-CoA
d. fatty acid, fatty acyl-AMP, fatty acyl-CoA, fatty acyl carnitine, fatty acyl-CoA
e. fatty acid, fatty acyl-phosphate, fatty acyl-CoA, fatty acyl carnitine, fatty acyl-CoA

1 double bond, no dehydrogenation

4. The complete beta-oxidation of oleoyl-CoA to acetyl-CoA would produce____(i)_____ NADH and _______(ii) $FADH_2$, while the complete beta-oxidation of stearoyl-CoA to acetyl-CoA would produce____(iii)_____ NADH and _______(iv) $FADH_2$?

a. (i) 9; (ii) 9; (iii) 9; (iv) 8
b. (i) 9; (ii) 8; (iii) 9; (iv) 9
c. (i) 8; (ii) 7; (iii) 8; (iv) 8
d. (i) 8; (ii) 8; (iii) 8; (iv) 7
e. (i) 8; (ii) 9; (iii) 9; (iv) 9

C18: 8 cycles of β oxidation
8 NADH 8 $FADH_2$
w/ 1 double bond
8 NADH 7 $FADH_2$

Name ____________________

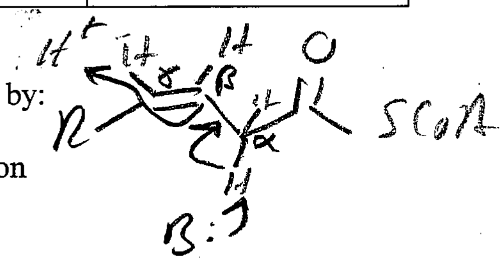
5. What is the correct order in which the following cofactors or substrates participate in beta oxidation, from first to last?

a. NAD^+, H_2O, FAD, CoASH
b. FAD, H_2O, NAD^+, CoASH
c. NAD^+, FAD, CoASH, H_2O
d. FAD, NAD^+, H_2O, CoASH
e. NAD^+, FAD, H_2O, CoASH

6. Match the enzyme from beta oxidation with an enzyme from the citric acid cycle that carries out the most similar chemistry

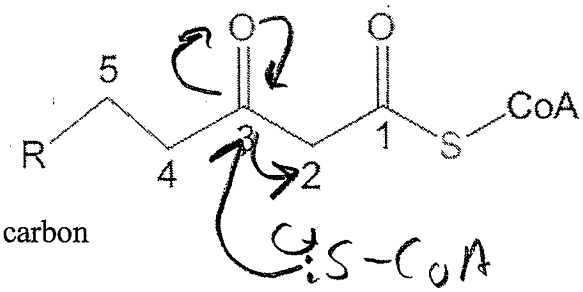
	β-hydroxyacyl-CoA dehydrogenase	Acyl-CoA dehydrogenase	Enoyl-CoA hydratase
(a)	~~Malate dehydrogenase~~	Succinate dehydrogenase	fumarase
(b)	Succinate dehydrogenase	α-ketoglutarate dehydrogenase	fumarase
(c)	Succinate dehydrogenase	Malate dehydrogenase	aconitase
(d)	Succinate dehydrogenase	Malate dehydrogenase	fumarase
(e)	Malate dehydrogenase	α-ketoglutarate dehydrogenase	aconitase

7. The reaction catalyzed by enoyl-CoA isomerase will be initiated by:



a. hydride transfer to the substrate alpha carbon
b. general base abstraction of a proton from the substrate beta carbon
c. hydride transfer to the substrate beta carbon
d. hydride transfer to the substrate gamma carbon
e. general base abstraction of a proton from the substrate alpha carbon

8. What will be the next electron pushing step in the catabolism of the following intermediate of beta oxidation?



a. hydride transfer from NADH to C3
b. hydride transfer from NADH to C5
c. general base abstraction of a proton from the C2 carbon
d. Attack of the thiolate of Coenzyme A on C3
e. Attack of the thiolate of Coenzyme A on C1

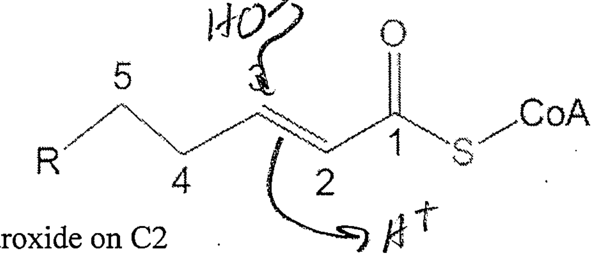
9. What is the correct sequence of reactions for conversion of propionyl-CoA to a metabolite that can enter the citric acid cycle?

a. (i) carboxylation, (ii) epimerization, (iii) isomerization
b. (i) carboxylation, (ii) isomerization, (iii) epimerization
c. (i) epimerization, (ii) carboxylation, (iii) isomerization
d. (i) carboxylation, (ii) dehydrogenation, (iii) isomerization
e. (i) carboxylation, (ii) isomerization, (iii) dehydrogenation

Prop CoA
↓
D MeMalonyl CoA
↓
L MeMalonyl CoA
↓
succinyl CoA

Name

10. What will be the next electron pushing step in the catabolism of the following intermediate of beta oxidation?



a. general base abstraction of a proton from water to form a hydroxide, followed by attack of the hydroxide on C2

b. general base abstraction of a proton from water to form a hydroxide, followed by attack of the hydroxide on C3

c. transfer of a hydride from NADH to C3

d. transfer of a hydride from NADH to C2

e. attack of the electron pair in the double bond on a water molecule

11. The structures of which of the following compounds shown to the right are collectively referred to as "ketone bodies"?

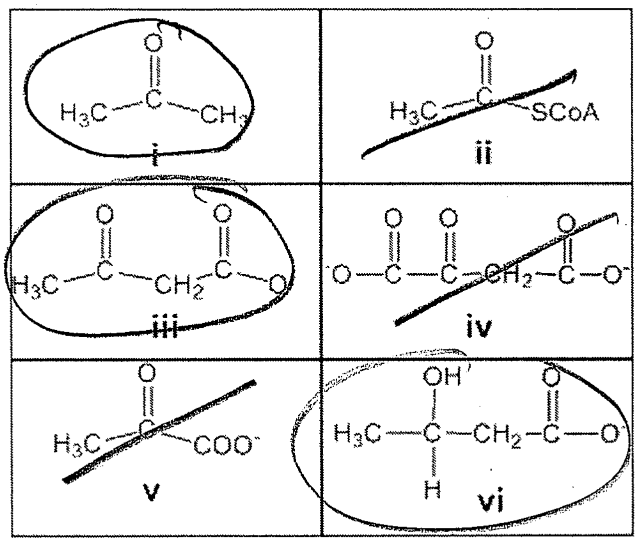
a. i, iii, and iv

b. i, iii, and vi

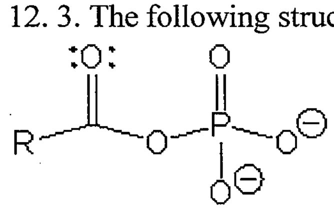
c. ii, iii, and vi

d. iii, v, and vi

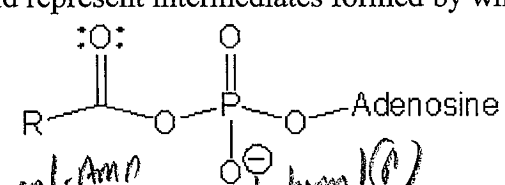
e. i, iv, and vi



12. 3. The following structures could represent intermediates formed by what enzymes?



(i)



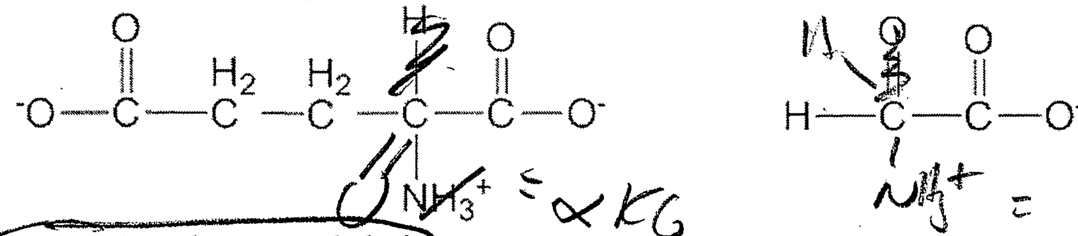
(ii)

forms acyl-AMP — AMP 9 to form 1(P) — forms carboxyphosphate

	Fatty acyl-CoA synthetase	Glutamine synthetase	Carbamoyl phosphate synthetase
(a)	(i)	(i)	(ii)
(b)	(ii)	(i)	(ii)
(c)	(ii)	(i)	(i)
(d)	(ii)	(ii)	(i)
(e)	(i)	(ii)	(i)

Name ______________________

13. The following compounds would be formed from the transamination of which two compounds?



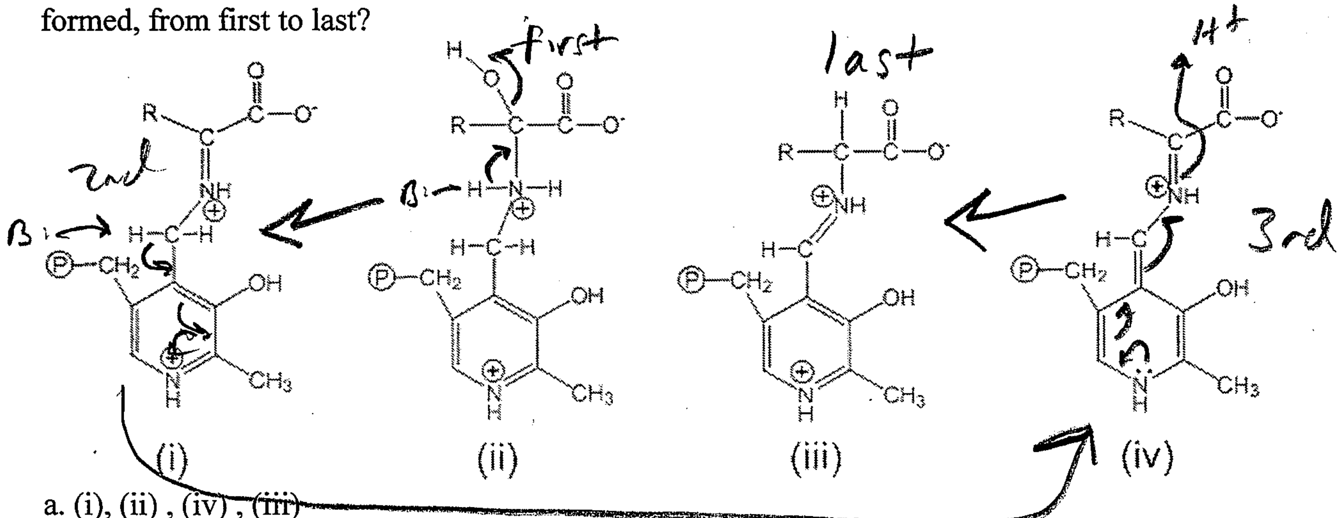
= αKG = glycine

a. alpha-ketoglutarate and glycine
~~b. oxaloacetate and glycine~~
c. oxaloacetate and alanine
d. alpha-ketoglutarate and alanine
e. alpha-ketoglutarate and serine

14. Conversion of glutamate to glutamine is catalyzed by a:
a. transaminase
b. hydrolase
c. synthetase
~~d. dehydrogenase~~
e. mutase

Glu + NH_4^+ + ATP → gln + ADP + Pi

15. Shown below are intermediates formed in the second half of a transamination reaction that will result in formation of an amino acid. What is the correct order in which these compounds are formed, from first to last?



a. (i), (ii), (iv), ~~(iii)~~
b. (ii), (i), (iii), (iv)
~~c. (iii), (ii), (iv), (i)~~
d. (ii), (i), (iv), (iii)
e. (iii), (iv), (i), (ii)

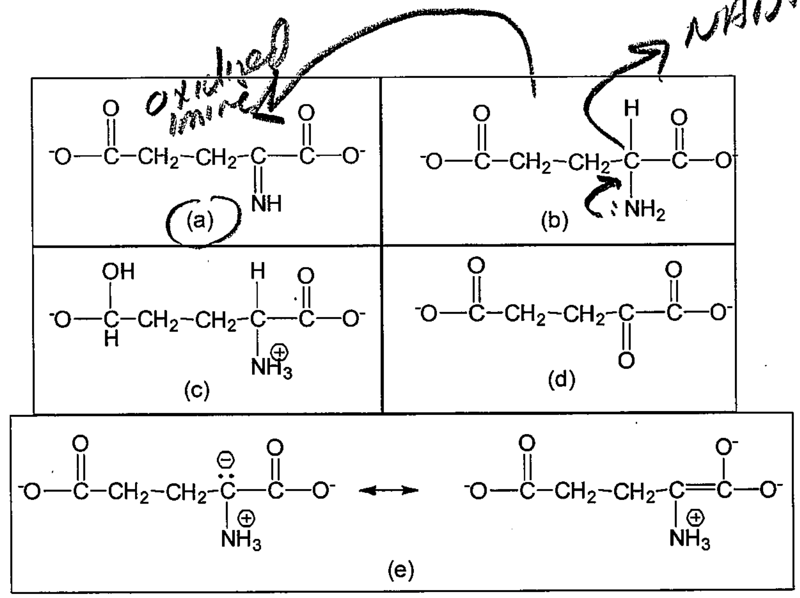
16. Under normal physiological conditions, amino groups are transferred from extrahepatic tissue to the liver in the form of __gln__. Under conditions of physiological stress (e.g. strenuous exercise) the amino groups might be transferred additionally in the form of __Ala__.
a. glutamate; alanine
b. alanine; glutamate
c. glutamine; alanine
d. glutamine; glutamate
e. glutamate; aspartate

Name ________________________

17. Which of the following processes does NOT involve oxidation and/or reduction of substrate molecule(s)?
(i) Transamination of aspartate and alpha-ketoglutarate — ox/red
(ii) Conversion of glutamate to glutamine — no ox/red
(iii) Deamination of glutamate to alpha-ketoglutarate — oxidation
(iv) Amination of bicarbonate to carbamoyl phosphate no ox/red

a. (i) and (iii)
b. (i) and (iv)
c. (ii) and (iii)
d. (i), (ii), and (iv)
e. (ii) and (iv)

18. The first ~~oxidized~~ intermediate in the reaction catalyzed by glutamate dehydrogenase will have which structure?



19. What nitrogenous compounds directly enter the Urea cycle and donate their amino groups for urea synthesis?
a. two ammonias
b. carbamoyl phosphate, aspartate
c. ammonia, glutamate
d. carbamoyl phosphate, glutamate
e. ammonia, aspartate

20. Of the following lists, which contains compounds that are ALL involved in the coupling of the citric acid and urea cycles?
a. fumarate, malate, ~~pyruvate~~, ~~alanine~~, aspartate
b. fumarate, ~~succinate~~, malate, glutamate, alpha-ketoglutarate
c. ~~succinate~~, malate, oxaloacetate, glutamate, aspartate
d. fumarate, malate, oxaloacetate, glutamate, aspartate
e. ~~succinate~~, malate, oxaloacetate, ~~pyruvate~~, aspartate

Name ________________________

21. What is the correct order for metabolites that are used in the activated methyl cycle (the cyclic pathway that allows methyl groups to be transferred to acceptors such as uracil). The abbreviations used are: SAM, S-adenosylmethionine; SAH, S-adenosylhomocysteine; THF, tetrahydrofolate; HC, homocysteine

Met → SAM $\xrightarrow{R}$ SAH → HC

R-CH_3

THF CH_3THF

a. SAM, SAH, Met, HC
b. Met, SAH,SAM, HC
c. Met, SAM, SAH, HC
d. SAM, Met, SAH, HC
e. SAH, Met, SAM, HC

22. An amino acid whose carbon skeleton is catabolized to acetoacetyl-CoA is keto(i)________, and an amino acid whose carbon skeleton is catabolized to is succinyl-CoA gluco(ii)________.
a. (i) glucogenic; (ii) glucogenic
b. (i) glucogenic; (ii) ketogenic
c. (i) ketogenic; (ii) glucogenic
d. (i) ketogenic; (ii) ketogenic

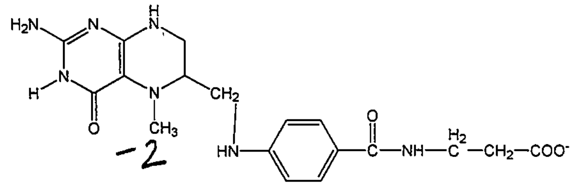
23. Which of the following reactions NEVER occurs during the mitochondrial Q cycle?
a. QH_2 reduces an FeS cluster OK
b. QH· reduces a protein bound cytochrome OK
c. QH· is reduced by using a protein bound cytochrome as e^- donor OK
d. Q is reduced by using a protein bound cytochrome as e^- donor
e. QH· reduces [redacted] soluble cytochrome C

24. C1 units for biosynthetic reactions in mammals are primarily derived from which amino acid?
a. alanine
b. glutamate
c. glutamine
*d. serine
e. aspartate

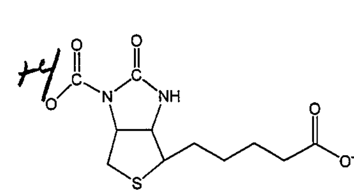
25. Which statement is correct about the reaction catalyzed by complex I of the electron transfer chain?
a. electrons are transferred in the form of a hydride ion directly from NADH to Coenzyme Q
b. electrons are transferred in the form of a hydride ion from NADH to FMN and then as a hydride to Coenzyme Q
c. electrons are initially transferred in the form of hydride ions from NADH to FeS cluster(s), which then transfer the electrons as single electrons to coenzyme Q
d. electrons are initially transferred in the form of hydride ions from NADH to FMN, and then transferred as single electrons from FMN to FeS cluster(s) and then coenzyme Q
e. electrons are initially transferred in the form of hydride ions from NADH to iron-sulfur cluster(s), and then transferred as single electrons from FeS cluster(s) to FMN and then coenzyme Q

Name ______________________

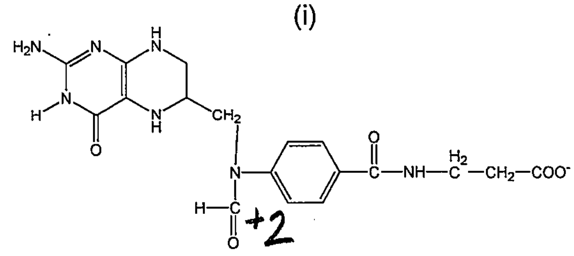
26. Correctly assign the oxidation states for the C1 groups being carried by the following molecules



(i)



(ii)



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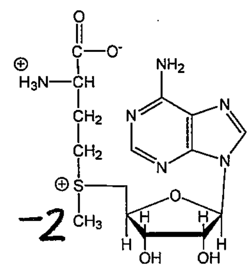

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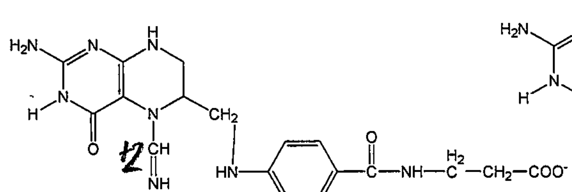
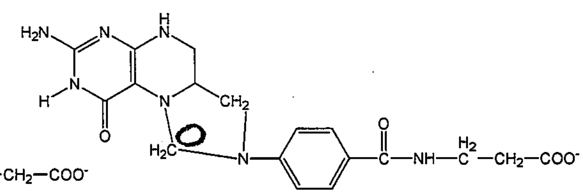


(v)



(vi)

	(i)	(ii)	(iii)	(iv)	(v)	(vi)
(a)	0	+3	+4	0	+3	+2
(b)	-2	+3	+2	-3	+2	0
(c)	-2	+3	+3	-2	+4	-2
(d)	-2	+4	+2	-2	+2	0
(e)	-2	+3	+2	-2	+4	-2

27. What is the proper name for complex II of the mitochondrial electron transfer chain?

a. succinate: ubiquinone oxidoreductase
b. succinate: FAD oxidoreductase
c. fumarate: $FADH_2$ oxidoreductase
d. succinate: NAD^+ oxidoreductase
e. succinate: O_2 oxidoreductase

28. Based on your knowledge of the reaction catalyzed by complex IV of the respiratory chain, which of the following is the best properly balanced "proton inventory" equation to describe what reaction complex IV catalyzes?

a. ~~$4CytC_{red} + O_2 + 6H^+_N \rightarrow 4CytC_{ox} + 2H_2O + 2H^+_P$~~
b. $4CytC_{red} + O_2 + 8H^+_N \rightarrow 4CytC_{ox} + 2H_2O + 4H^+_P$
c. $2CytC_{red} + O_2 + 4H^+_N \rightarrow 2CytC_{ox} + H_2O + 4H^+_P$
d. $4CytC_{red} + O_2 + 4H^+_N \rightarrow 4CytC_{ox} + 2H_2O$
e. $2CytC_{red} + 2O_2 + 8H^+_N \rightarrow 2CytC_{ox} + 2H_2O + 4H^+_P$

$4H^+$ pumped
$4H^+$ consumed
$O_2 + 4H^+ \rightarrow 2H_2O$

cI pumps 4e⁻
cIII pumps 2e⁻
cIV pumps 4e⁻

Name ______________________

29. How many protons are pumped per electron pair transferred to molecular oxygen for electron pairs derived from the reactions catalyzed by the following enzymes?

	Succinate dehydrogenase	pyruvate dehydrogenase	Fatty acyl-CoA dehydrogenase	β-hydroxyacyl-CoA dehydrogenase
(a)	6	9	9	6
(b)	6	10	10	6
(c)	III & IV 6	I, III, IV 10	III, IV 6	I, III, IV 10
(d)	4	8	8	4
(e)	10	10	6	6

30. Which of the following molecules NEVER crosses the inner mitochondrial membrane
a. ATP, ADP, Pi yes
b. pyruvate, Coenzyme A, NAD^+ yes
c. ADP, Coenzyme A, NAD^+ yes
d. Coenzyme A, NAD
e. None of the above can cross the inner mitochondrial membrane; the metabolite pools are completely isolated.

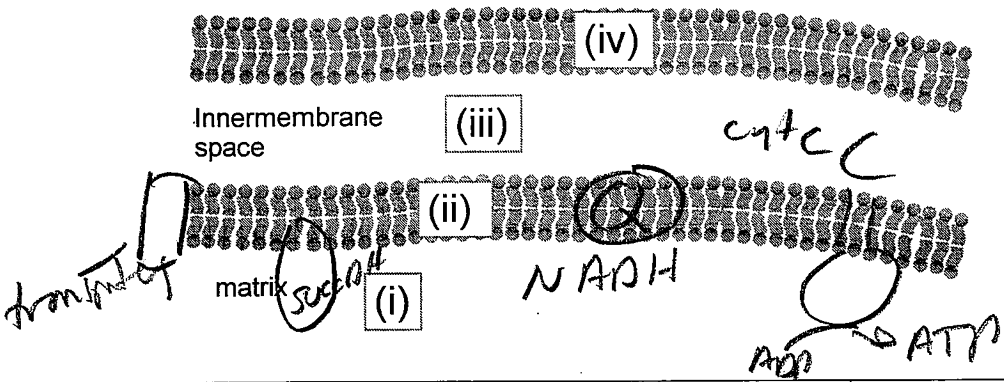
31. Which of the following events occur in the mitochondrial matrix in the reactions of the malate-aspartate shuttle?
(i) oxidation of malate to OAA Y
(ii) reduction of OAA to malate N
(iii) transamination of glutamate and OAA Y
(iv) transamination of alpha-ketoglutarate and aspartate N
(v) import of alpha-ketoglutarate and export of glutamate N
(vi) import of malate and export of alpha-ketoglutarate Y
(vii) import of aspartate and export of glutamate N Y
(viii) import of glutamate and export of aspartate Y

a. (i), (iv), (vi), (viii)
b. (ii), (iii), (vi), (vii)
c. (i), (iv), (v), (viii)
d. (ii), (iv), (v), (vii)
e. (i), (iii), (vi), (viii)

32. The ATP synthase consists of two components: F_1, which is a(n) _peripheral_(i)_____membrane protein complex and whose function is ___(ii)_synthesis___, and F_0, which is a(n) __Integral_(iii)____membrane protein complex and whose function is ____(iv)_H+ move_.

a. (i) integral	(ii) proton movement	(iii) peripheral	(iv) ATP synthesis
b. (i) integral	(ii) ATP synthesis	(iii) peripheral	(iv) proton movement
c. (i) peripheral	(ii) ATP synthesis	(iii) integral	(iv) proton movement
d. (i) peripheral	(ii) proton movement	(iii) integral	(iv) ATP synthesis

33. The following is a representation of the portions of the mitochondrion important in metabolism, respiration and oxidative phosphorylation. In which locations will the following components of these processes reside for proper catalysis to occur?



	NADH (i)	ATP and ADP (i)	ubiquinone (ii)	Cytochrome C (iii)	Succinate dehydrogenase (ii)	Pyruvate translocase (ii)	adenine nucleotide translocase (ii)
(a)	(i)	(i)	(ii)	(iii)	(ii)	(ii)	(ii)
(b)	(iii)	(i)	(ii)	(i)	(ii)	(iv)	(iv)
(c)	(i)	(i)	(ii)	(iii)	(ii)	(iv)	(iv)
(d)	(i)	(iii)	(ii)	(i)	(i)	(ii)	(ii)
(e)	(iii)	(i)	(ii)	(iii)	(ii)	(iv)	(iv)

34. What effects will the following compounds have on the rate of ATP synthesis (no effect, slow down, stop completely) after several minutes exposure to isolated mitochondria oxidizing succinate? Compare each set of choices before choosing the best available answer.
(i) a protonophore stop
(ii) a potassium ionophore slow
(iii) rotenone (an inhibitor of complex I) no effect
(iv) cyanide (inhibitor of complex IV) stop

	(i) protonophore	(ii) K^+ ionophore	(iii) rotenone	(iv) cyanide
(a)	slow down	stop	stop	no effect
(b)	slow down	no effect	no effect	stop
(c)	slow down	stop	stop	stop
(d)	stop	slow down	no effect	no effect
(e)	stop	slow down	no effect	stop

35. After you answer this question you are done with the new material section. So here is the question. How are you feeling?
a. great, looking forward to the second half of the exam!
b. this is a lot of information…
c. I love biochemistry!
d. I can't wait to be done
e. do I get credit for marking any answer for this question?

Name ______________________

COMPREHENSIVE SECTION $pKa = 6$ = A^- form

36. You have an aqueous 0.250 M solution of the amino acid histidine at pH 6.25. What is the concentration of the form of histidine that bears a net charge of "0"?
a. 0.14 M
b. 0.11 M
c. 0.0064 M
d. ~~0.155 M~~ 0.090M
e. 0.16 M

$pH = pKa + \log \frac{A^-}{HA}$; $\frac{A^-}{HA} = 10^{pH-pKa} = 1.78$

$A^- = 1.78(HA)$

$A^- + HA = 0.25$; $1.78HA + HA = 0.25$; $HA = 0.090$ M

$A^- = 0.25 - 0.090$
$= 0.160$

37. What are the values that belong at the indicated positions in the purification table shown below?

Purification table for a new enzyme						
step of purification	volume (ml)	total protein (mg)	total activity (units)	specific activity (units/mg)	% recovery	fold purification
lysate	1000	20,000	15,000	0.75		
ammonium sulfate precipitation	100	6,000	10,000	(i)		
ion exchange	200	1,000	8,000		(ii)	
gel filtration	25	200	4,000	20		(iii)

$\frac{10,000}{6000} = 1.7$

$\frac{8000}{15000} \times 100 = 53\%$

$20/0.75 = 27$

	(i)	(ii)	(iii)
(a)	1.7	53	27
(b)	10	20	20
(c)	1.7	5.0	3.8
(d)	10	53	20
(e)	0.60	20	27

38. You purify an enzyme from a crude bacterial lysate. The protein runs as a single band on nondenaturing polyacrylamide gel electrophoresis (PAGE) and as three distinct bands on SDS-PAGE. The sizes of the three protein bands on SDS-PAGE are 70,000, 50,000 and 10,000, and the staining intensities of the proteins indicate they are present in a stoichiometric ratio of 3:3:2, respectively. Your protein elutes from a size exclusion (gel permeation) column with an apparent molecular weight of 1,140,000. The quaternary structure of your protein is what (recall α is largest subunit, γ the smallest):

$70 \times 3 + 50 \times 3 + 10 \times 2 = 380,000$

a. $\alpha_3\beta_3\gamma_2$
b. $\alpha_6\beta_6\gamma_4$
c. $\alpha_9\beta_9\gamma_6$
d. ~~$\alpha_4\beta_4\gamma_2$~~
e. $\alpha_9\beta_6\gamma_4$

$\frac{1,140,000}{380,000} = 3$

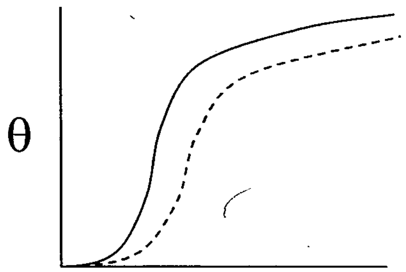
$(\alpha_3\beta_3\gamma_2) \times 3 = \alpha_9\beta_9\gamma_6$

Name ________________________

39. Which bonds correctly correspond to the phi, psi and peptide bonds of a polypeptide chain?

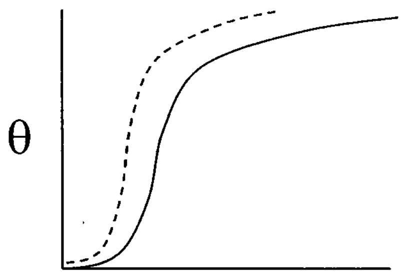
	phi	psi	peptide
(a)	$C_{(carbonyl)}$-N	C_α-N	C_α- $C_{(carbonyl)}$
(b)	C_α-N	C_α- $C_{(carbonyl)}$	$C_{(carbonyl)}$-N
(c)	$C_{(carbonyl)}$-N	C_α- $C_{(carbonyl)}$	C_α-N
(d)	C_α-N	$C_{(carbonyl)}$-N	C_α- $C_{(carbonyl)}$
(e)	C_α-N	$C_{(carbonyl)}$-N	C_α- $C_{(R)}$

40. For the two graphs shown below, the solid lines represent the oxygen dissociation curves observed for hemoglobin under a certain set of conditions, while the dashed lines represent the dissociation curves observed after changing a parameter. Which parameter change will give the indicated dissociation curve?



$[O_2]$

(i) shift R(i)



$[O_2$

(ii) shift R(i) shift L (ii)

	increase $[CO_2]$	decrease pH	decrease [DPG]
(a)	(ii)	(i)	(i)
(b)	(ii)	(i)	(ii)
(c)	(i)	(ii)	(i)
(d)	(i)	(i)	(ii)
(e)	(ii)	(ii)	(i)

41. For the amino acid aspartate, the presence of a fixed negative charge in close proximity to the side chain ionizable group will ____(i)_______ the pKa of the side chain. For the amino acid histidine, the presence of a fixed positive charge in close proximity to the side chain ionizable group will ____(ii)_______ the pKa of the imidazole ring.

stabilize neutral so lower pKa

a. (i) ~~increase;~~ (ii) increase
b. (i) increase; (ii) decrease
c. (i) decrease; ~~(ii) increase~~
d. (i) decrease; (ii) decrease

Asp

stabilize neutral form, so > pKa

42. Kinetic analysis of a homodimeric enzyme of 150,000 molecular weight (that is the Mr of the dimer) catalyzing conversion of substrate S to product P provides the following kinetic constants: V_{max} = 1000 units when 1 mg of enzyme is assayed. Assume each subunit contains an active site; i.e. there are two active sites per dimer. Calculate the turnover number for this enzyme on the basis of monomeric units (i.e. per active site).

a. 1,250 s^{-1}
~~b. 2,500 s^{-1}~~
c. 5,000 s^{-1}
d. 18,000 s^{-1}
e. 9,000 s^{-1}

$$\left(\frac{1{,}000\ \mu mol\ product}{min \cdot mg\ E}\right)\left(\frac{150{,}000\ mg\ E}{mmol\ E}\right)\left(\frac{1\ mmol\ E}{1000\ \mu mol\ E}\right)\left(\frac{1\ min}{60\ s}\right) \times \left(\frac{1\ \mu mol\ E}{2\ \mu mol\ active\ sites}\right)$$

Name ____________________

43. Match the following levels of protein structure with the appropriate partner.

i.	A regular, recurring arrangement in space of adjacent amino acid residues in a polypeptide chain 2^o
ii.	spatial relationship between all amino acids in polypeptide; the 3-D structure of the polypeptide 3^o
iii.	A simple combination of a few 2° elements with a specific geometric arrangement motif
iv.	a polypeptide chain or part of a polypeptide chain that can independently fold into a stable tertiary structure domain

	(i)	(ii)	(iii)	(iv)
(a)	Secondary	Domain	Motif	tertiary
(b)	Motif	tertiary	Domain	Domain
(c)	Secondary	Motif	tertiary	Domain
(d)	Motif	quaternary	tertiary	Secondary
(e)	Secondary	tertiary	Motif	Domain

44. In an alpha helix, an intrachain hydrogen bond is formed between residue n and residue __(i)___; in a three-stranded beta sheet, how many hydrogen bonds are formed, on average, per amino acid residue on each outer strand __(ii)__?

	(i)	(ii)
(a)	n + 3	1
(b)	n + 4	1
(c)	n + 5	1
(d)	n + 3	2
(e)	n + 4	2

45. Algebraically solve the Michaelis-Menten equation for [S] to answer the following question: what concentration of substrate gives an initial rate of 1200 units for an enzyme that exhibits a V_{max} of 5000 units and a K_m of 2 mM?

a. 0.48 mM
b. 0.63 mM
c. 0.24 mM
d. 0.76 mM
e. 0.52 mM

$v = \frac{V_{max}[S]}{K_m + [S]}$; $v \cdot K_m + v \cdot [S] = V_{max}[S]$

$(V_{max} - v)[S] = v \cdot K_m$

$[S] = \frac{v \cdot K_m}{V_{max} - v}$

$= \frac{1200 \times 2}{5000 - 1200}$

$=$

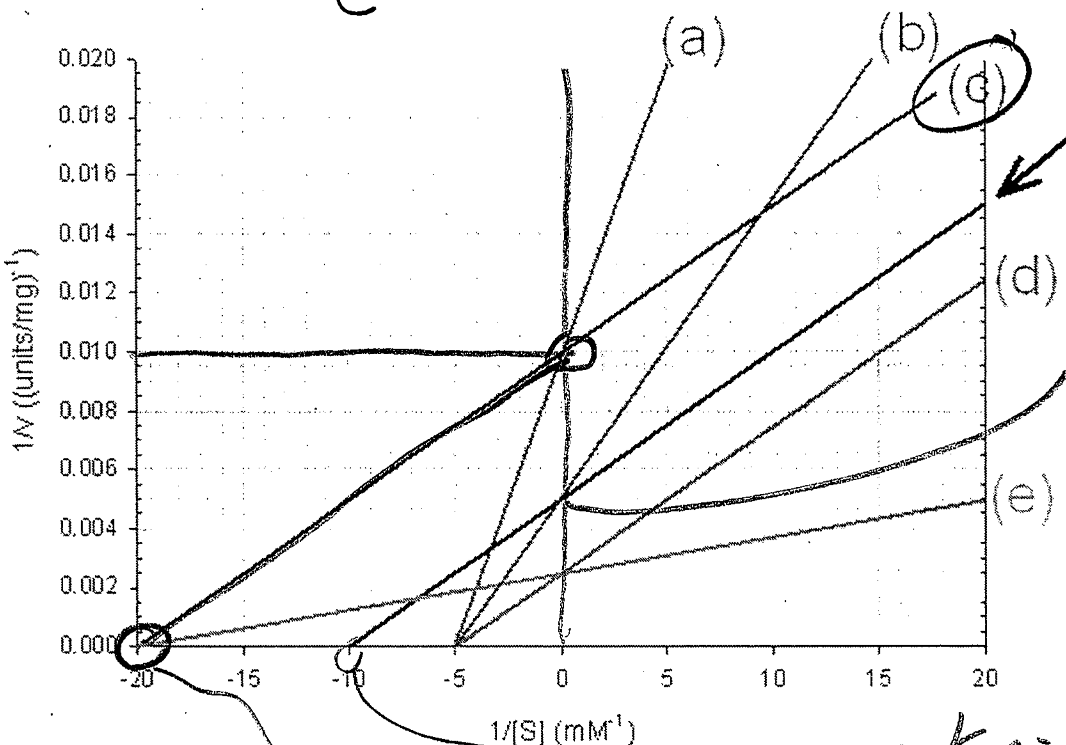
46. For the hydrolysis of an ester involving the formation of a tetrahedral intermediate, a metal ion would facilitate the formation of the intermediate via charge ____(i)_______. For the hydrolysis of ATP, the initial attack of water on the phosphorus of ATP would be facilitated by charge _____(ii)______.

a. (i) shielding; (ii) stabilization
b. (i) stabilization; (ii) shielding
c. (i) shielding; (ii) shielding
d. (i) stabilization; (ii) stabilization

Name ______________________

47. The following graph shows a Lineweaver-Burke (**1/v** vs. **1/[S]**) plot (indicated by an arrow) for an enzymatic reaction transforming substrate S to product P. Which line represents the effect of a reversible inhibitor present at a concentration that would decrease the apparent V_{max} by 2-fold while decreasing the apparent K_m by 2-fold.

C



Vmax = 1/0.005 = 200

new Vmax = 100

1/new Vmax = 0.01

Km = 1/10 = 0.1

new Km = 0.05 so 1/Km = 20

48. 10. Which of the following are correct statements about Schiff base formation and function during catalysis

(i) creates an electrophilic center T

(ii) creates a nucleophilic center F

(iii) stabilizes carbanion formation T

(iv) stabilizes carbocation formation F

(v) serves as a general acid/base F

(vi) resonance stabilization of a reaction intermediate T

a. (ii), (iv), and (v)

b. (i), (iv) and (vi)

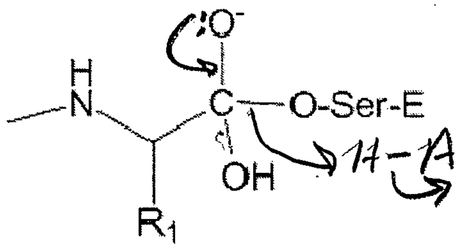
c. (i), (iii) and (vi)

d. (ii), (iii), and (iv)

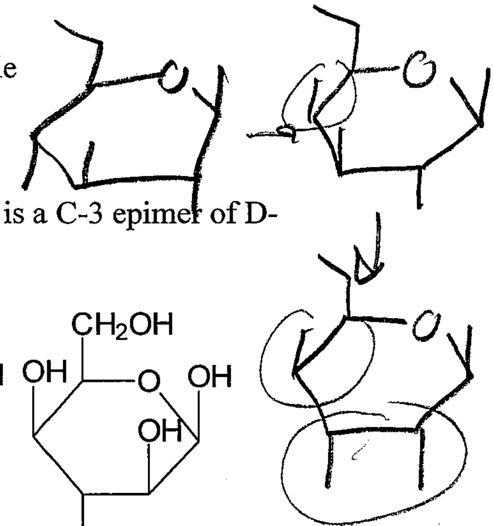
e. (iii), (v) and (vi)

Name ____________________

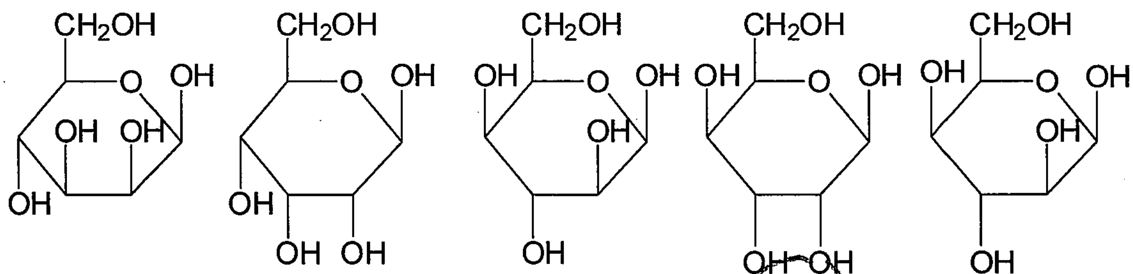
49. The following is a substrate or intermediate formed during chymotrypsin-catalyzed polypeptide hydrolysis. The transformation of this compound to the next intermediate or product will involve:



a. general base catalysis
b. general acid catalysis
c. metal ion catalysis
d. nucleophilic attack using an amino acid side chain as the nucleophile
e. nucleophilic attack using water as the nucleophile



50. What is the structure of beta-D-gulopyranose, given that D-gulose is a C-3 epimer of D-galactose, and D-galactose is a C-4 epimer of D-glucose.



(a) (b) (c) (d) (e)

51. What sugar linkages and repeating units are present in the following polysaccharides?
Abbreviations: Glc = glucose; NAG = N-acetylglucosamine; NAM = N-acetylmuramic acid;
(I) cellulose β 1,4
(II) glycogen α1,4 + α1,6
(III) peptidoglycan β1,4 NAMNAG
(IV) chitin β1,4 NAG

	(I)	(II)	(III)	(IV)
(a)	α-(1,4)-D-Glc	β-(1,4)- and β-(1,6)- D-Glc	β-(1,4)-D-NAG	β-(1,4)-D-NAM-D-NAG
(b)	β-(1,4)-D-Glc	α-(1,4)- and α-(1,6)- D-Glc	β-(1,4)-D-NAG	β-(1,4)-D-NAM-D-NAG
(c)	β-(1,4)-D-Glc	α-(1,4)- and α-(1,6)- D-Glc	β-(1,4)-D-NAM-D-NAG	β-(1,4)-D-NAG
(d)	α-(1,4)-D-Glc	β-(1,4)- and β-(1,6)- D-Glc	β-(1,4)-D-NAM-D-NAG	β-(1,4)-D-NAG
(e)	β-(1,4)- and β-(1,6)- D-Glc	α-(1,4)- and α-(1,6)- D-Glc	β-(1,4)-D-NAG	β-(1,4)-D-NAM-D-NAG

Name ____________________________

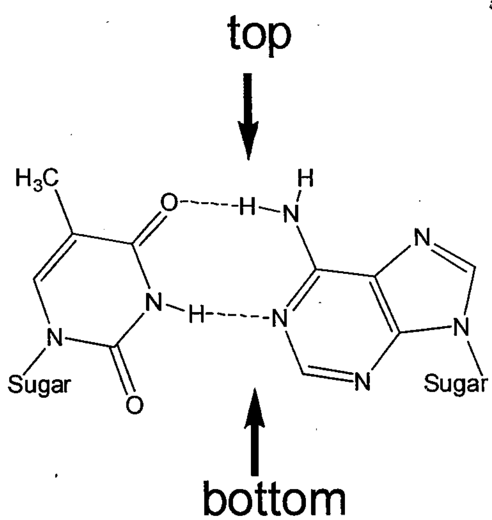
52. Which of the following is not a correct statement of Chargaff's rules?
a. DNA base composition differs from one species to another
b. DNA base composition is identical in different individuals and different tissues of same species
c. DNA base composition does not change with age, nutritional status, or changing environment
d. The sum of A + T equals the sum of G + C for all samples of DNA F
e. All of the above statements are correct

A+G = C+T

53. For the Watson-Crick base pair shown below, the base shown to the left is a ___(i)_____ and the minor groove is on the ________(ii)________ face.

pyrimidine

bottom



a. (i), purine ; (ii) bottom
b. (i), pyrimidine ; (ii) bottom
c. (i), purine ; (ii) top
d. (i), pyrimidine ; (ii) top

54. In Watson-Crick DNA, the base orientation is ____anti____, the sugar pucker is ____C2' endo____ and the two strands are ____anti //____.
a. anti; C2' exo; antiparallel
b. ~~syn; C2' endo; antiparallel~~
c. anti; C2' endo; antiparallel
d. ~~anti; C2' exo; parallel~~
e. syn; C2' exo; antiparallel

55. Order the following fatty acids from lowest to highest melting point.
(i) Linoleic acid
(ii) Linolenic acid
(iii) Oleic acid
(iv) Stearic acid

more double bonds lowest

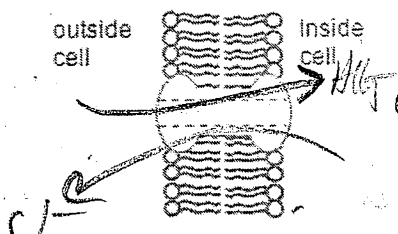
ii < i < iii < iv

a. (i) > (ii) > (iii) > (iv)
b. (iii) > (i) > ~~> (iv) > (ii)~~
c. (ii) > (i) > (iii) > (iv)
d. ~~(iv) > (iii) > (i) > (ii)~~
e. (iv) > (ii) > (i) > (iii)

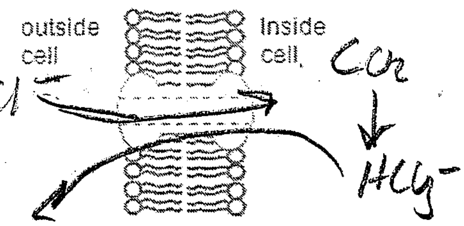
Name ____________________________

56. When relatively large concentrations of fatty acids are placed in solution they form structures called _____(i)_______. When relatively large concentrations of phospholipids are placed in solution they form structures called ________(ii)________.
a. (i) liposomes; (ii) liposomes
b. (i) micelles (ii) micelles
c. (i) liposomes (ii) micelles
d. (i) micelles (ii) liposomes

57. In which direction are Cl^-, and HCO_3^- transported for the chloride-bicarbonate exchanger when red blood cells are in the following tissues, and in what direction does carbonic anhydrase (CA) operate within the cell?



(i) In erythrocyte in blood vessels in the lung



(ii) In erythrocyte in blood vessels in muscle tissue

	(i)	(ii)
(a)	HCO_3^- goes in , Cl^- goes out, CA converts HCO_3^- to CO_2	HCO_3^- goes out , Cl^- goes in, CA converts CO_2 to HCO_3^-
(b)	HCO_3^- goes out , Cl^- goes in, CA converts CO_2 to HCO_3^-	HCO_3^- goes in , Cl^- goes out, CA converts HCO_3^- to CO_2
(c)	HCO_3^- goes in , Cl^- goes out, CA converts CO_2 to HCO_3^-	HCO_3^- goes out , Cl^- goes in, CA converts HCO_3^- to CO_2
(d)	HCO_3^- goes out , Cl^- goes in, CA converts HCO_3^- to CO_2	HCO_3^- goes in , Cl^- goes out, CA converts CO_2 to HCO_3^-
(e)	HCO_3^- goes in , Cl^- goes out, CA converts HCO_3^- to CO_2	HCO_3^- goes out , Cl^- goes in, CA converts HCO_3^- to CO_2

58. Order the following sequence of events properly for the Na^+-K^+ ATPase-facilitated movement of Na^+ and K^+ ions from the FIRST to the LAST step. Place any two steps that logically occur together in the same step.

(i) Phosphorylation of the transporter protein using a phosphate group donated from ATP (2)
(ii) phosphoryl group removal from the transporter (4)
(iii) Binding of K^+ ions (3)
(iv) binding of Na+ ions (1)
(v) release of K^+ ions (5)
(vi) release of Na^+ ions

a. (i) > (iv) > (vi) and (iii) > (ii) > (v)
b. (iv) > (i) > (vi) and (iii) > (ii) > (v)
c. (i) > (iii) and (iv) > (ii) > (v) and (vi)
d. (iv) > (iii) > (i) > (ii) > (v) and (vi)
e. (iii) and (iv) > (i) > (ii) > (v) and (vi)

Name ________________________

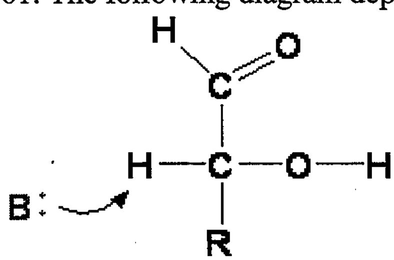
59. Which of the following is NOT one of the contributors to the large free energy observed for the hydrolysis of ATP to ADP

a. Relief of electrostatic repulsion
b. Product ionization
c. Product hydrolysis
d. Resonance stabilization
e. Product solvation

60. What is the general name for enzymes that catalyze the transfer of a phosphoryl group from one position to another within the same molecule?

a. phosphatase
b. kinase
c. nucleotidyl transferase
d. phosphodiesterase
e. mutase

61. The following diagram depicts the initial step for which type of reaction?



a. aldol condensation
b. claisen condensation
c. aldo-keto isomerization
d. dehydration
e. alcohol dehydrogenation

62. The reactions of glycolysis beginning with glucose and ending with pyruvate consume ___(i)_2_ ATP molecules, form _____(ii)_4____ ATP molecules via substrate level phosphorylation, and form ___(iii)_2_ NADH molecules.

a. (i) 2; (ii) 2; (iii) 4
b. (i) 2; (ii) 4; (iii) 4
c. (i) 1; (ii) 2; (iii) 1
d. (i) 2; (ii) 2; (iii) 2
e. (i) 2; (ii) 4; (iii) 2

Name ________________________

63. Given the information in the table below, calculate the free energy change for the transfer of a phosphoryl group from 1,3-diphosphoglycerate to ADP to form ATP and 3-phosphoglycerate.

Standard free energies for hydrolysis of selected phosphoryl groups	
Reaction (not necessarily charge-balanced)	$\Delta G'^{\circ}$ (kJ/mol)
phosphoenolpyruvate + $H_2O \rightarrow$ pyruvate + P_i	-61.9
1,3-diphosphoglycerate + $H_2O \rightarrow$ 3-phosphoglycerate + P_i	-49.3
ATP + $H_2O \rightarrow$ AMP + PP_i	-45.6
Phosphocreatine + $H_2O \rightarrow$ creatine + P_i	-43.0
ADP + $H_2O \rightarrow$ AMP + P_i	-32.8
ATP + $H_2O \rightarrow$ ADP + P_i	-30.5
Glucose-1-phosphate + $H_2O \rightarrow$ glucose + P_i	-20.9
PP_i + $H_2O \rightarrow$ 2 P_i	-19.2
Glucose-6-phosphate + $H_2O \rightarrow$ glucose + P_i	-13.8
Glycerol-3-phosphate + $H_2O \rightarrow$ glycerol + P_i	-9.2

a. -18.8 kJ/mol
b. ~~+18.8 kJ~~/mol
c. +79.8 kJ/mol
d. -79.8 kJ/mol

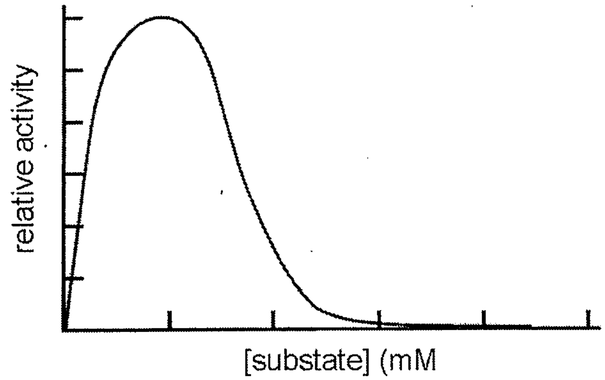
1,3 DPG → 3PG + Pi   - 49.3
ADP + Pi → ATP   +30.5
-18.8

64. For the reactions of glycolysis, a schiff base adduct is formed by the enzyme _____(i)________, a thioester adduct is formed by the enzyme _________(ii)_______________, and a phosphoenzyme adduct is involved in the enzyme ____________(iii)_______________ .
Abbreviations used: GAPDH, glyceraldehyde-3-phosphate dehydrogenase; TIM, triose phosphate isomerase
a. (i) aldolase; (ii) GAPDH; (iii) hexokinase
b. (i) TIM; (ii) GAPDH; (iii) phosphoglycerate mutase
c. (i) aldolase; (ii) TIM; (iii) hexokinase
d. (i) aldolase; (ii) TIM; (iii) enolase
e. (i) aldolase; (ii) GAPDH; (iii) phosphoglycerate mutase.

65. 12. The substrate level phosphorylation reactions in glycolysis use which high energy compound(s) as the direct phosphoryl group donors in forming nucleoside triphosphates?
a. acyl phosphate and phosphoguanidine
b. acyl phosphate, enolphosphate
c. ~~acyl phosphate~~, thioester
d. enolphosphate, and phosphoguanidine
e. alkyl , enolphosphate

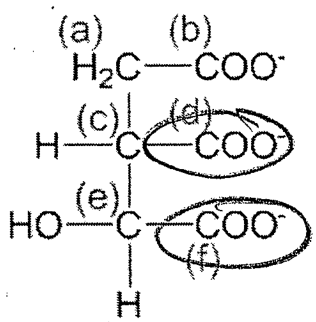
Name ____________________________

66. The following v vs. S plot would be observed for the enzyme ___(i)____ where the substrate being varied is ______(ii)______.



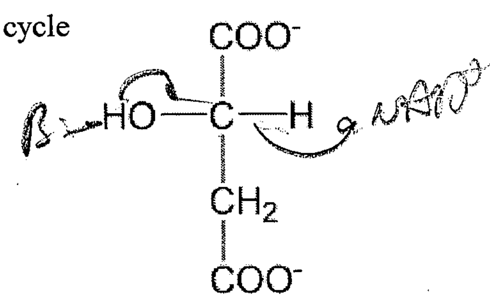
a. (i), hexokinase (ii), ATP
b. (i), pyruvate dehydrogenase (ii), pyruvate
c. (i), phosphofructokinase (ii), fructose-6-phosphate
d. (i) hexokinase (ii), glucose
e. (i), phosphofructokinase (ii), ATP

67. Which carbon atoms of isocitrate (indicated by letters (a) through (f)) are released as CO_2 during one turn of the citric acid cycle?



a. (a) and (b)
b. (b) and (d)
c. (b) and (f)
d. (d) and (f)
e. two of (b), (d) or (f)

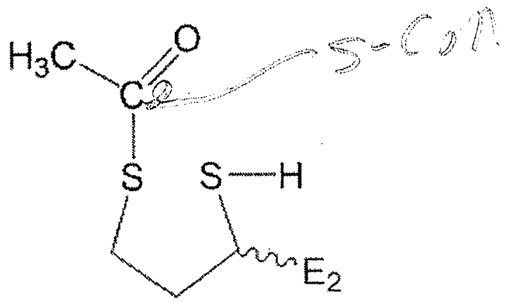
68. The transformation of the substrate shown at right in the citric acid cycle will be initiated by:



a. Abstraction of the C2 proton by a general base
b. Abstraction of the hydroxyl proton by a general base
c. Abstraction of a proton on C3 by a general base
d. Hydride abstraction from C2 of malate
e. Hydride abstraction from the hydroxyl of malate

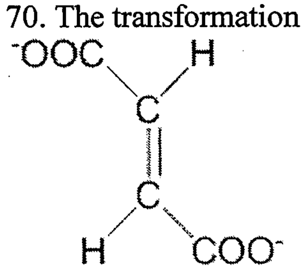
Name ______________________

69. During the reaction catalyzed by pyruvate dehydrogenase, what will occur in the next step for the intermediate shown below?



a. general base abstraction of a proton from the thiol of lipoamide
b. attack of the thiolate of deprotonated CoA on the thiol of lipoamide that is bound to the acetyl group
c. attack of the thiolate of deprotonated CoA on the free thiol of lipoamide
d. attack of the thiolate of deprotonated CoA on the carbonyl C of the adduct
e. general base abstraction of a proton from the methyl group to form a resonance stabilized carbanion

70. The transformation of the following substrate in the citric acid cycle will be initiated by:



a. nucleophilic attack of a hydroxide ion on C2 or C3
b. General base abstraction of a proton from fumarate
c. Reduction of the C-C double bond
d. removal of one of the carboxyl groups