 Name ____________________________

Biochemistry 5700
Fall, 2003
Exam 3

INSTRUCTIONS:

You have two hours to take the exam. The exam should have 11 questions. Answer all questions legibly and completely in the space provided Good Luck!!

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

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

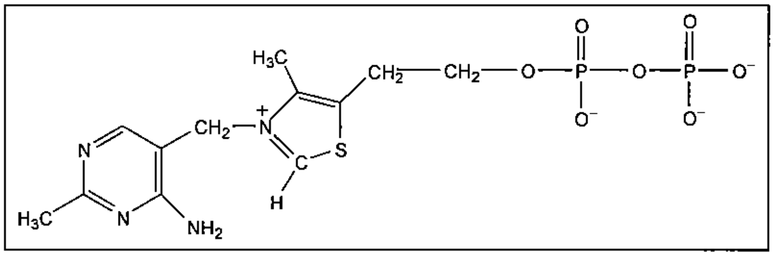
Distribution for Exam 3

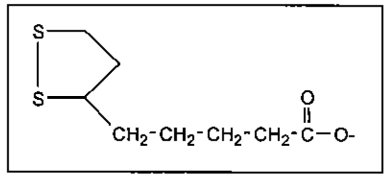
Statistics: Exam 3

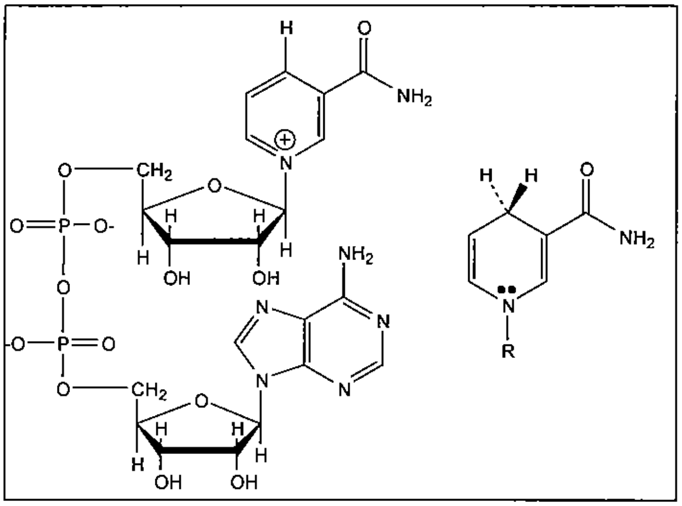
Graded out of: 100.00 Highest grade: 98.00 Mean grade: 65.55 Standard deviation: 21.09
Number of records: 62 Lowest grade: 10.00 Median grade: 65.00

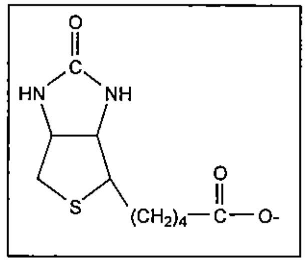
Score Range	Frequency
[0, 5)	
[5, 10)	
[10, 15)	2
[15, 20)	
[20, 25)	
[25, 30)	1
[30, 35)	3
[35, 40)	3
[40, 45)	
[45, 50)	4
[50, 55)	4
[55, 60)	5
[60, 65)	5
[65, 70)	8
[70, 75)	2
[75, 80)	5
[80, 85)	3
[85, 90)	9
[90, 95)	6
[95, 100)	2
[100]	

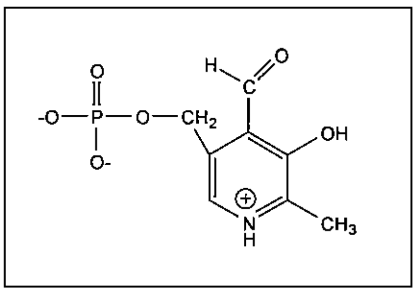
Fewer Bars **More Bars**

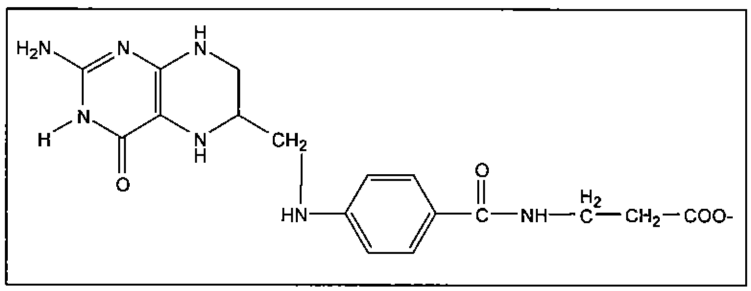


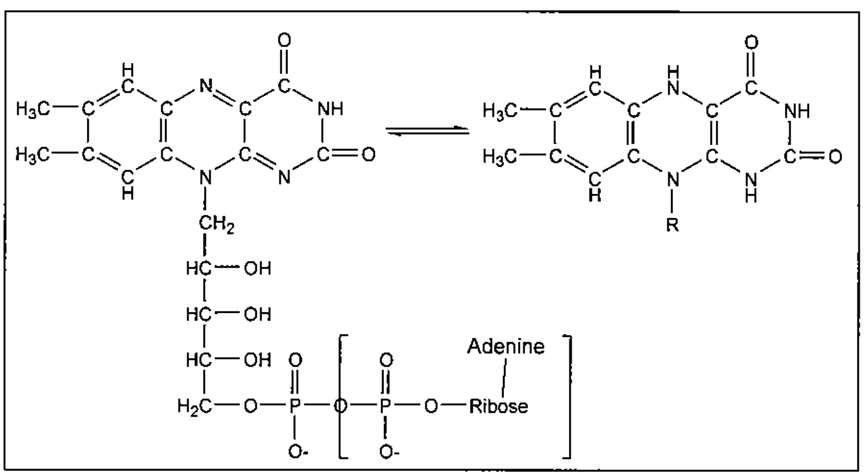


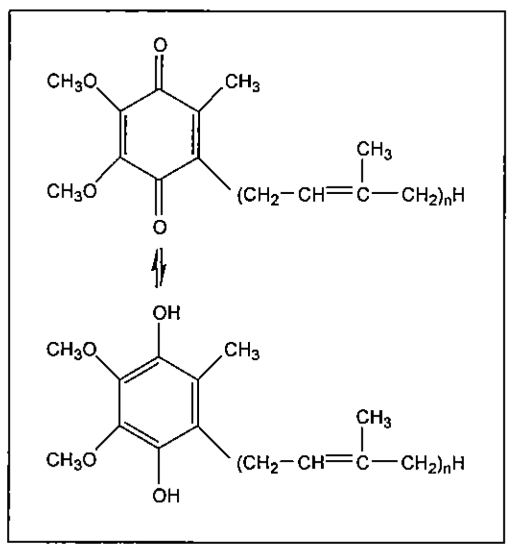












Name Key

(1) (10 points) For each of the following, name a specific "transporter" representing that type, and name the molecule(s) transported:

Transport type	Name of transporter	molecule(s)
(a) passive uniport	glucose permase	glucose
(b) passive antiport	Cl^-/HCO_3^- exchanger	Cl^-/HCO_3^-
(c) primary active transport: ATP driven	Na^+-K^+ ATPase	Na^+, K^+
(d) primary active transport: light driven	bacteriorhodopsin	H^+
e) secondary active transport	lactose permease	lactose, H^+

(2) (4 points) What are the differences between a transporter and an ion channel?

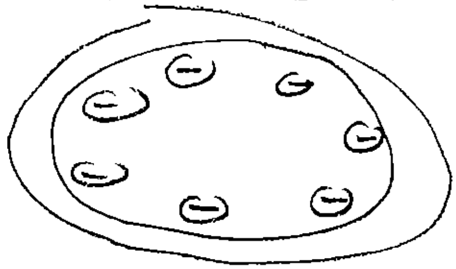
transporter- saturable, like an enzyme

ion channel - not saturable, very high rate, rapid gating (on/off)

(3) (4 points) What is the physiological role of the sodium-potassium ATPase?

To bring K^+ into cell & expel Na^+ according to rxn: $3Na^+_{in} + 2K^+_{out} \rightarrow 3Na^+_{out} + 2K^+_{in}$

This results in net ⊖ charge inside cell, giving cell the desired electrochemical potential

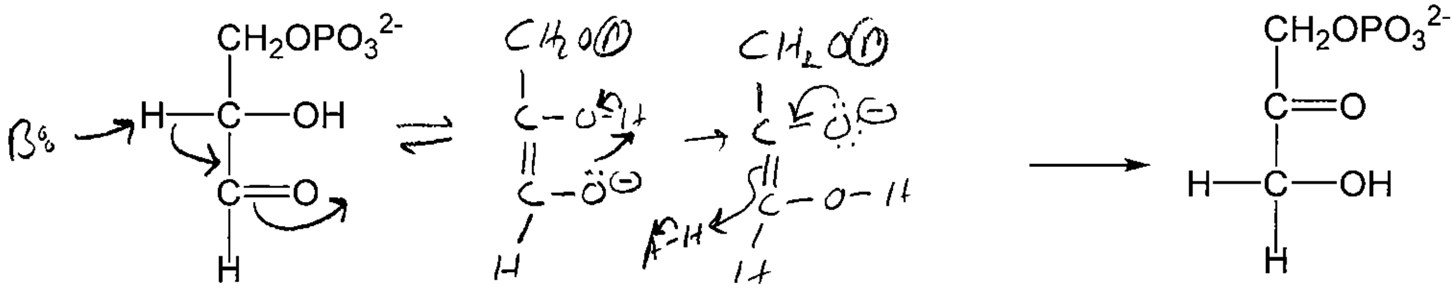


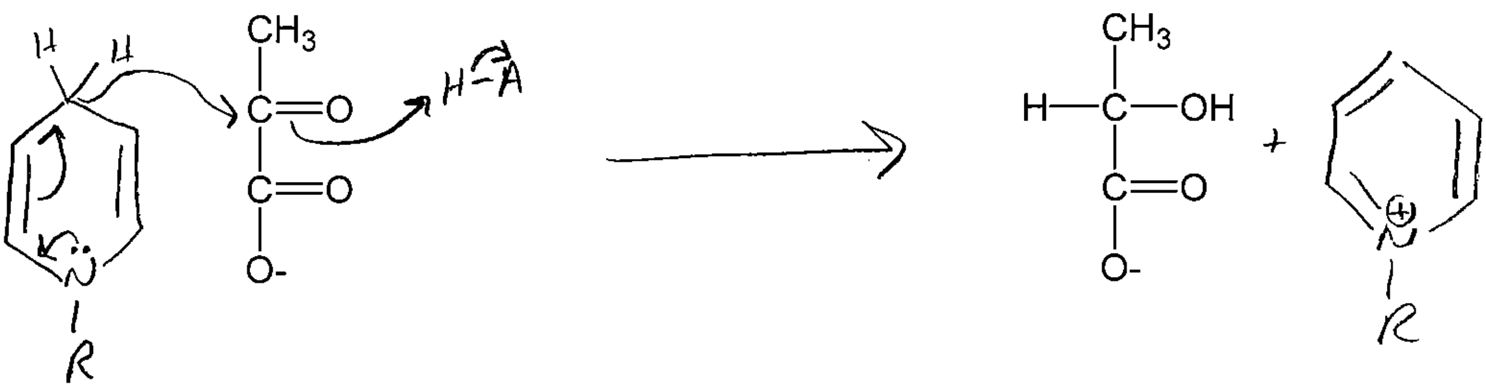
 Name Key

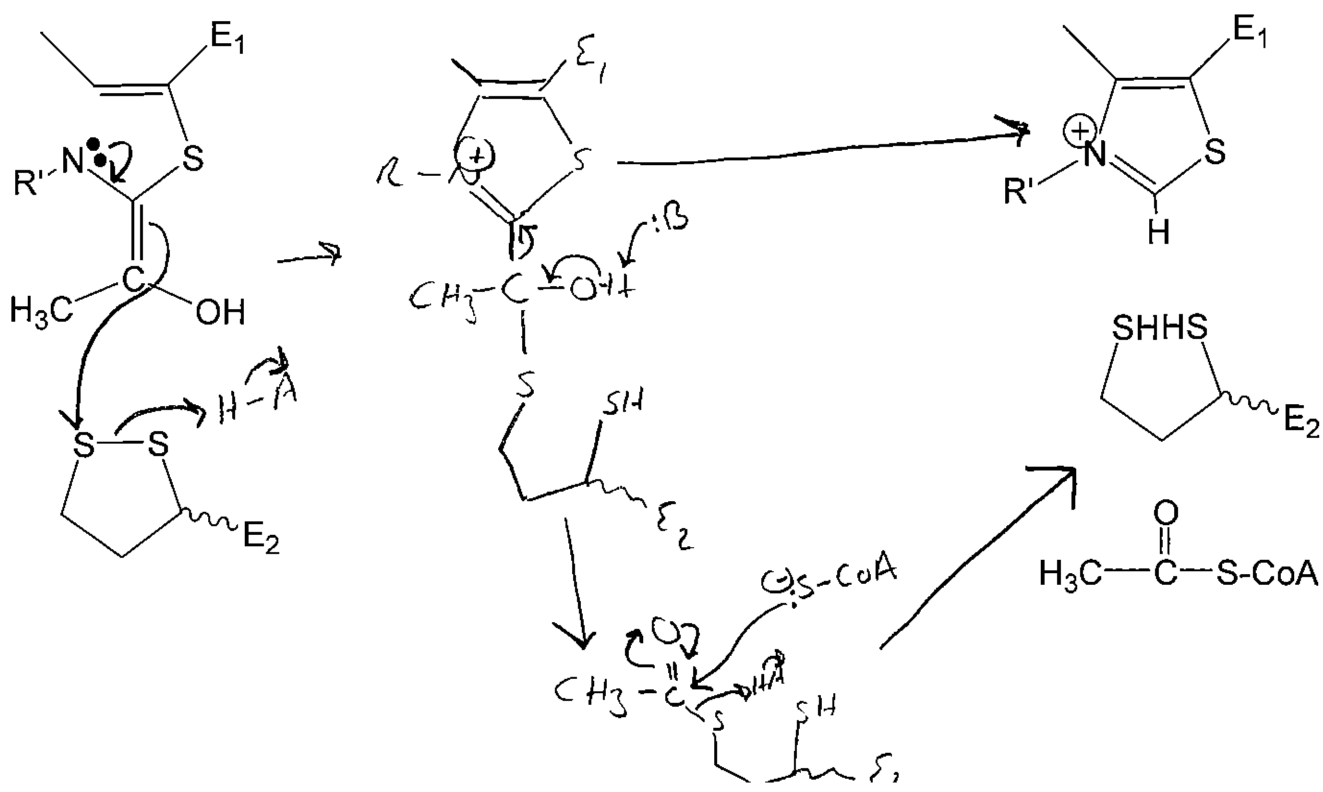
(4) (20 points) For the following general classes of reaction, name a specific enzyme from central metabolism catalyzing that type of reaction, write the complete reaction catalyzed by the enzyme (note- structures and mechanism are not required-just names), and list any cofactor(s) used by that enzyme.

Reaction type	Enzyme	Balanced equation with necessary cofactor(s) listed above arrow
claisen condensation	Citrate synthase	acetyl-CoA + oxaloacetate + H_2O → citrate + CoA
elimination	enolase fumarase	2-phosphoglycerate ⇌ phosphoenolpyruvate L-malate ⇌ fumarate
intramolecular phosphoryl transfer	phospho-glucomutase phosphoglycerate mutase	Glc-6-P ⇌ Glc-1-P 3-(P)-glycerate ⇌ 2-(P)-glycerate
aldo-keto isomerization	triose phosphate isomerase phosphohexose isomerase	dihydroxyacetone-(P) ⇌ glyceraldehyde-3-(P) Glc-6-(P) ⇌ Frc-6-(P)
substrate-level phosphorylation	phosphoglycerate kinase pyruvate kinase succinyl-CoA synthetase	1,3-di(P) glycerate + ADP ⇌ ATP + 3(P) glycerate PEP + ADP ⇌ Pyruvate + ATP SuccCoA + GDP ⇌ Succinate + GTP
FAD-dependent dehydrogenation (no other cofactors)	Succinate dehydrogenase	Succinate + FAD ⇌ fumarate + $FADH_2$
NAD^+-dependent dehydrogenation (no other cofactors)	Lactate DH malate DH glyceraldehyde-3-(P) DH; isocitrate DH, etc.	pyruvate + NADH ⇌ L-lactate + NAD^+ L-malate + NAD^+ ⇌ Oxaloacetate + NADH
nonoxidative alpha-keto acid decarboxylation	pyruvate decarboxylase	Pyruvate $\xrightarrow[\text{pyrophosphate}]{\text{thiamine}}$ CO_2 + acetaldehyde
oxidative alpha-keto acid decarboxylation	pyruvate DH or α-ketoglutarate DH	pyruvate (αKG) + NAD^+ + CoA $\xrightarrow{\text{FAD, lipoic acid, TPP}}$ acetyl-CoA (or succ CoA) + CO_2 + NADH
NADP+-dependent dehydrogenation	glc-6-(P) DH 6-(P)-gluconate DH	Glc-6-(P) + $NADP^+$ ⇌ 6-(P)-gluconolactone + NADPH 6-(P) gluconate + $NADP^+$ → ribulose-5-(P) + NADPH + CO_2

(5) (15 points) Complete the enzyme-catalyzed reaction mechanisms (from left to right), with appropriate intermediates, acids/bases, cofactors, and electron pushing arrows:





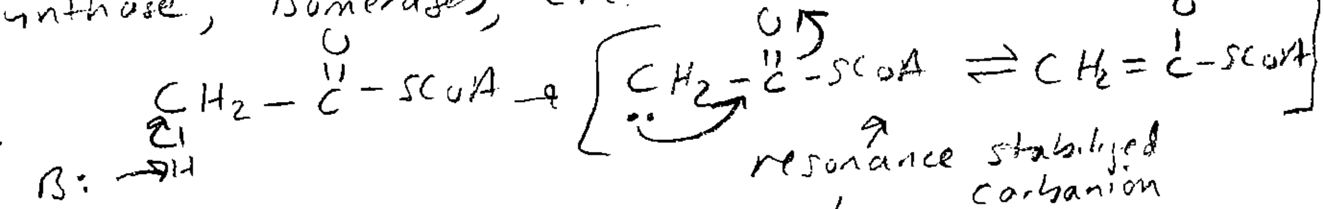


 Name Key

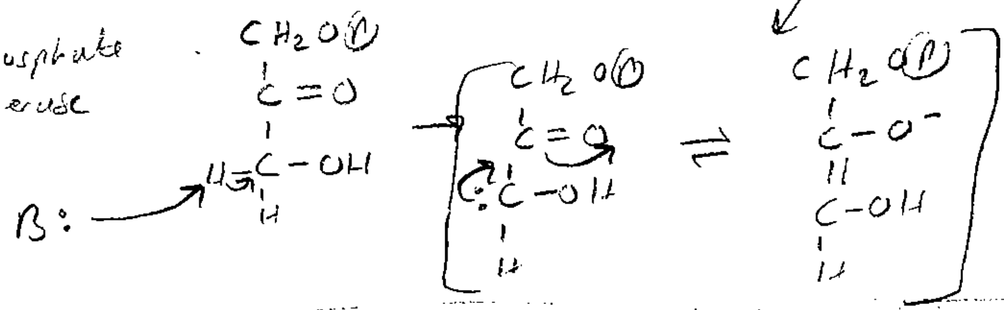
(6) (12 points) The ability to stabilize carbanions is an important feature of many metabolic enzymes. What are two different strategies an enzyme might employ, in the absence of an exogenous cofactor like TPP, to stabilize a carbanion generated during catalysis? Use specific examples from glycolysis and/or the citric acid cycle in answering the question.

(1) Keto-enol tautomerization, such as seen in citrate synthase, isomerases, etc.

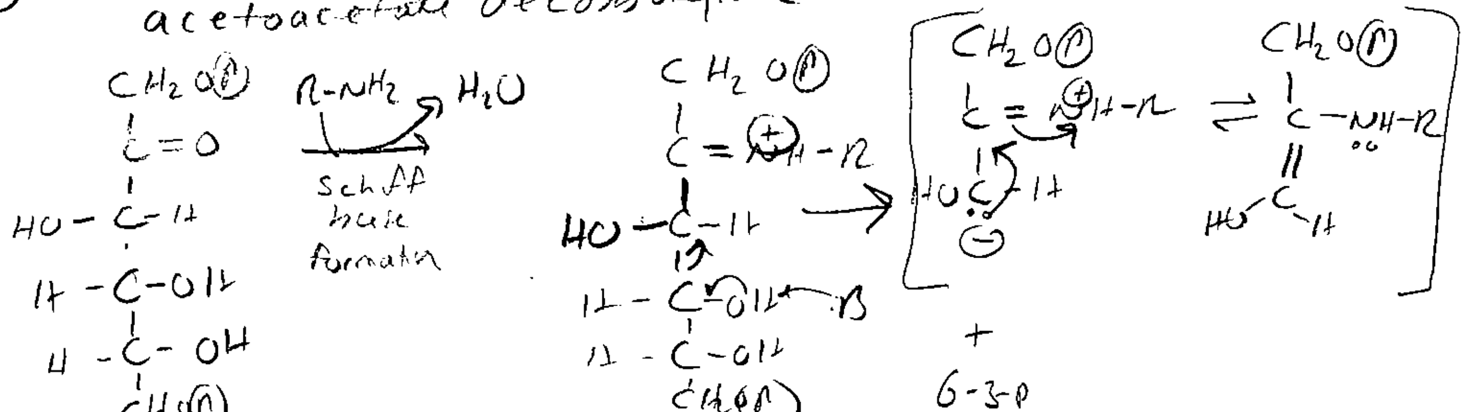
citrate synthase:



triose phosphate isomerase



(2) Schiff base/cationic imine as an e⁻-sink, eg aldolase, acetoacetate decarboxylase



(7) (6 points) Write the balanced chemical equations for fermentation of glucose to (a) lactate and (b) CO2 and ethanol.

a) glucose + 2ADP + 2Pi → 2 lactate + 2ATP

b) glucose + 2ADP + 2Pi → 2 EtOH + $2CO_2$ + 2ATP + $2H_2O$

(8) (4 points) Write the balanced chemical equation for one turn of the citric acid cycle (starting with acetyl-CoA).

Ac-CoA + $3NAD^+$ + $1FADH_2$ + GDP + Pi ⇌ $2CO_2$ + 3NADH + $1FADH_2$ + 1GTP + CoA

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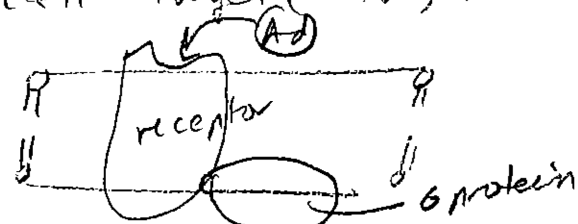
(9) (10 points) Describe the sequence of events involved in the hormonally-controlled mobilization of stored glycogen as an energy source.

- Adrenaline (epinephrine, glucagon) is produced in adrenal gland & released into blood stream
- adrenaline binds receptor protein on membrane of cell target (liver, muscle)



- adrenaline binding causes conf. change in G protein, causing it to release GDP + bind GTP
- Gprotein - GTP complex binds adenyl cyclase, activating this membrane enzyme
- Adenyl cyclase converts ATP → cAMP
- cAMP binds & activates protein kinase A
- protein kinase A phosphorylates phosphorylase kinase, thereby activating it
- phosphorylase kinase phosphorylates glycogen phosphorylase, activating it
- glycogen phosphorylase phosphorylyzes glycogen → glc-1-P

(10) (4 points) Glycogen phosphorylase in the liver is a glucose/AMP (circle one) sensor, and binds this metabolite in the phosphorylated/unphosphorylated (circle one) form. In contrast, glycogen phosphorylase in the muscle is a glucose/AMP (circle one) sensor and binds this metabolite in the phosphorylated/unphosphorylated (circle one) form.

 Name Key

(11) (11 points) Some chemoautotrophic bacteria gain all their energy from the oxidation of ammonia to nitrite (a **six electron** process). In theory at least (biochemical standard state conditions), the free energy provided by the oxidation of one mol NH_3 in the presence of O_2 is sufficient to form how many mols of ATP?.
($E^{\circ\prime}$ = +0.34 V for the NO_2^-/NH_3 couple, $E^{\circ\prime}$ = +0.816 V for the O_2/H_2O couple, $\Delta G^{\circ\prime}$ = -30.5 kJ/mol for ATP hydrolysis)

$$NH_3 + \cancel{2H_2O} \rightarrow NO_2^- + \cancel{6e^-} + \cancel{7H^+} \quad \mathcal{E}^{\circ\prime} = -0.34V$$

$$3\left(2H^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow H_2O\right) \quad \mathcal{E}^{\circ\prime} = +0.816V$$

$$\cancel{6H^+} + \tfrac{3}{2}O_2 + \cancel{6e^-} \rightarrow \cancel{3H_2O}$$

$$NH_3 + \tfrac{3}{2}O_2 \rightarrow H_2O + NO_2^- + H^+ \quad \mathcal{E}^{\circ\prime} = +0.476V$$

$$\Delta G^{\circ\prime} = -nF\mathcal{E}^{\circ\prime} = -(6)\left(96.5\frac{kj}{V\cdot mol}\right)(0.476V)$$

$$\Delta G^{\circ\prime} = -275.6\ kj/mol$$

$$\frac{275.6\ \frac{\cancel{kj}}{mol\ NH_3}}{30.5\ \frac{\cancel{kj}}{mol\ ATP}} = \boxed{9.0\ \frac{mol\ ATP}{mol\ NH_3}}$$