CHEM 527 SECOND EXAM FALL 2006

YOUR NAME: KEY

NOTES:

1. Where appropriate please show work – if in doubt show it anyway.

2. Pace yourself – you may want to do the easier questions first.

3. Please note the point value of questions – adjust your answers and effort accordingly.

4. Some questions may have more data than you need.

5. Please be brief – focus your answers to the space provided.

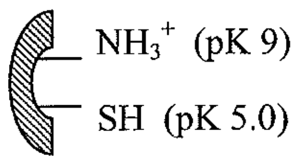
6. Please write CLEARLY – if I cannot read it – it is wrong.

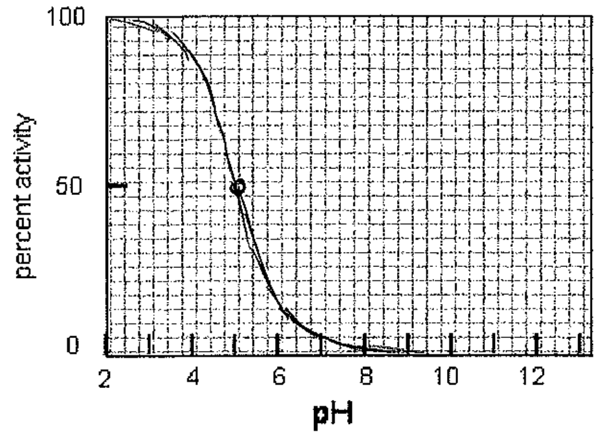
7. You are welcome to detach the metabolic chart but please don't decimate your exam in the process.

8. **Good luck.**

Question 1 (6 pts.). Draw clear accurate graphs to describe the behavior of the following systems. Clarity and accuracy rewarded.

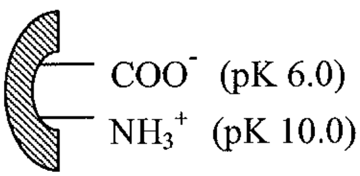
a. only the form of the enzyme show below is active. Show its pH dependence at the right.

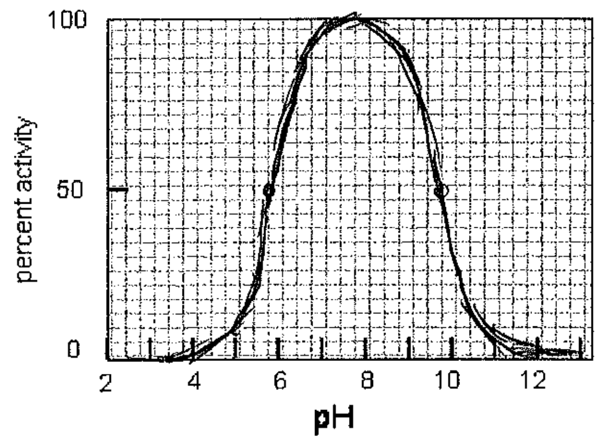




(3)

b. only the form of the enzyme show below is active. Show its pH dependence at the right.





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Question 2. (15 pts.). Short problems. Show work, but most credit goes to the correct numerical answer.

a. An enzyme has a V_{max} of 1.2 μmol/min and a rate of 0.12 μmol/min at 0.3 mM substrate. What is the K_m for the substrate K_m = 2.7 mM 3

$$v = 0.12 = \frac{1.2 \times 0.3\,mM}{K_m + 0.3\,mM}$$

$$K_m + 0.3\,mM = 3\,mM$$

$$v = \frac{V_{max} \cdot [S]}{K_m + [S]}$$ 1pt

b. In "a" above the molecular weight of the substrate and enzyme were 120 and 28,000 g/mol respectively and the amount of enzyme used was 56 μg. What is the maximal turnover number?

3

$$TN = \frac{1.2 \times 10^{-6}\ mol/min}{56 \times 10^{-6}\ g / 28{,}000\ g/mole}$$

TN = 600 /min

c. A single subunit (monomeric) oxygen binding protein shows a K_D of 5 mm. What is the fractional saturation at 15 mm partial pressure of oxygen?

$\theta = \frac{[O_2]}{K_D + [O_2]}$ or $\frac{pO_2}{K_D + pO_2}$

Fractional saturation 0.75 (3)

$\frac{15\,mM}{5 + 15\,mM}$

d. To answer this question, you will need some of the following: temperature = 37 °C; the oxygen concentration dissolved in pH 7.4 buffer in equilibrium with air is 0.22 mM; hemoglobin is saturated with oxygen at this concentration

One liter of solution containing 2 x 10^{-3} mol **hemoglobin** is gently stirred in air until equilibrium is reached. What is the total concentration of oxygen in the solution? (3)

2 mM hemoglobin ≡ max of 8 mM bound O_2

Total concentration = 8.22 mM

8.22×10^{-3} M

What is the free concentration of oxygen in this hemoglobin solution = 0.22 mM (3)

0.22×10^{-3} M

Same as 0.22

Question 3 (5 pts.). What is the effect of the following on hemoglobin or myoglobin. Circle the most appropriate answer. NC = no change.

Increasing pH on the oxygen affinity of hemoglobin	*increase*	*NC*	*decrease*
Decreasing pH on CO_2 binding to hemoglobin	*increase*	*NC*	*decrease*
Decreasing pH on DPG affinity of hemoglobin	*increase*	*NC*	*decrease*
Increasing DPG levels on CO_2 affinity of hemoglobin	*increase*	*NC*	*decrease*
Increasing DPG levels on O_2 affinity of myoglobin	*increase*	*NC*	*decrease*

K

Question 4 (8 pts.). Given the following calculate ΔG°' for equation 1:

1.	C	↔	A	ΔG°' = +3 kcal
2.	C	↔	B	ΔG°' = +6 kcal
3.	A	↔	B	ΔG°' = +3 kcal

C ↔ B +6 kcal
B ↔ A −3 kcal
+3

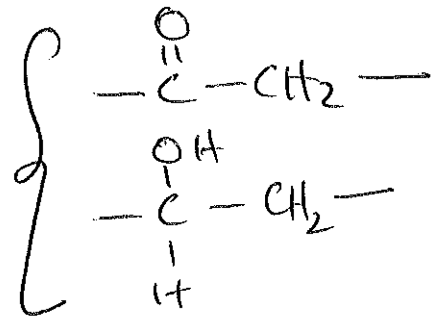
4pts

In equation 1 ... To make **ΔG more negative** I would: **circle all of the following which will definitely accomplish this:**

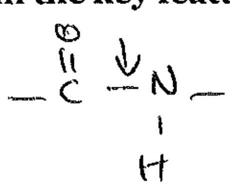
2 ea for "2" & "3"
−1 each incorrect from 4 to 0

1. increase the concentration of **A**
2. decrease the concentration of **A**
3. increase the concentration of **C**
4. decrease the concentration of **C**
5. increase the temperature
6. decrease the temperature
7. lower the pH
8. increase the pH
9. add the enzyme that catalyzes the reaction: C ↔ A
10. Dilute the mixture of C and A with an equal volume of water.

Question 5 (5 pts.). Draw the structure of a chemically-credible reversible inhibitor of an HIV-protease. Circle the functional group that is the key aspect of the anticipated inhibition.

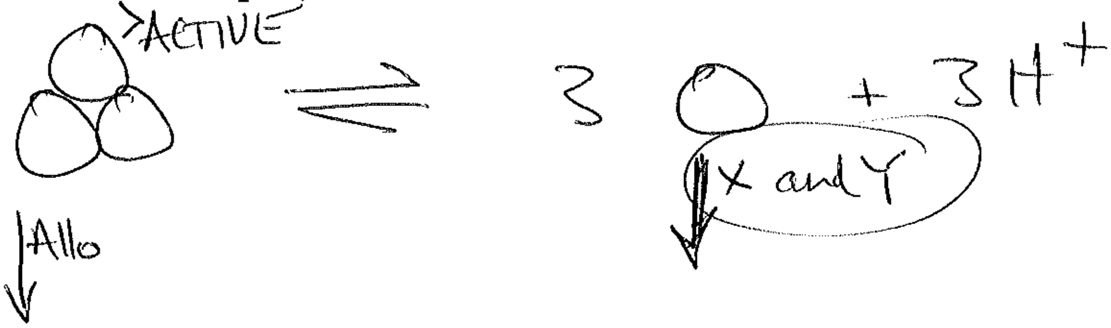
3 Any peptide which incorporates 
a equivalent
at scissile bond!

Now explain the key feature of the proposed inhibitor:

2 the  is replaced w/ a non-hydrolyzable functionality

K

Question 6 (8 pts.). Linked equilibria. Suppose that an enzyme is a trimer of identical subunits in equilibrium with monomers. The two substrates of the enzyme X and Y bind 5 times more tightly to the monomer. The trimer is 10-times more active than the monomer. An allosteric molecule binds preferentially to the trimer. Finally dissociation of trimer to monomers releases 3 protons into solution at pH 7.

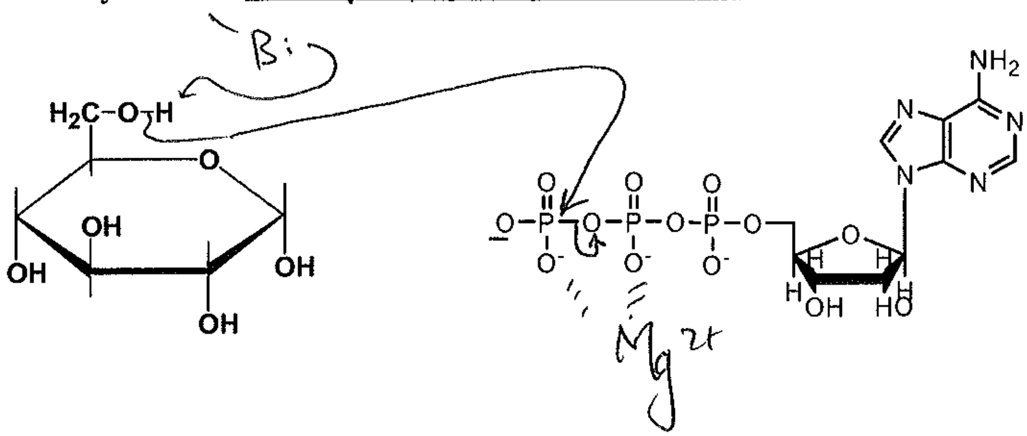


Circle the most appropriate answer for the following. What is the effect of:

a. Increasing [Y] on extent of monomers	**increase**	**NC**	**decrease**
b. Lowering pH to 6.0 on percentage of trimer	**increase**	**NC**	**decrease**
c. Raising the concentration of the allosteric molecule on enzyme activity	**increase**	**NC**	**decrease**
d. Lowering total enzyme concentration on the percentage of trimer	**increase**	**NC**	**decrease**

Questions 7 (8 pts.). For the following two parts. Place the name of the relevant enzyme in the space and draw a curved arrow representation of the reaction it catalyzes.

a. Enzyme name hexo kinase



K

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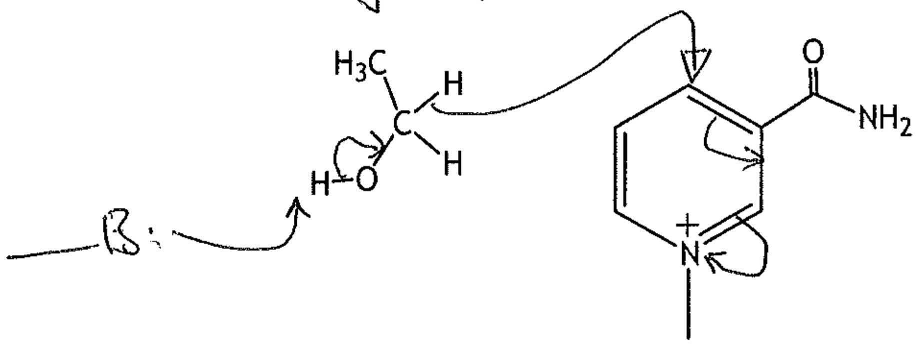
b. Enzyme name alcohol dehydrogenase



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Question 8 (6 pts.). Yield of ATP. In the space provided give the yield of ATP that would be formed in the following processes (enter a number from 0-10):

a. per molecule of dihydroxyacetone phosphate to ethanol 2

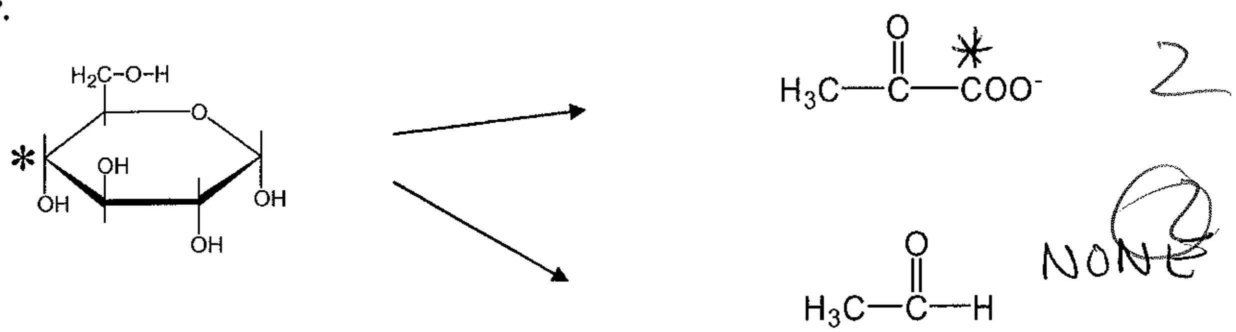
b. per molecule of fructose 6-P converted to lactate 3

c. per molecule of fructose converted to ethanol 2

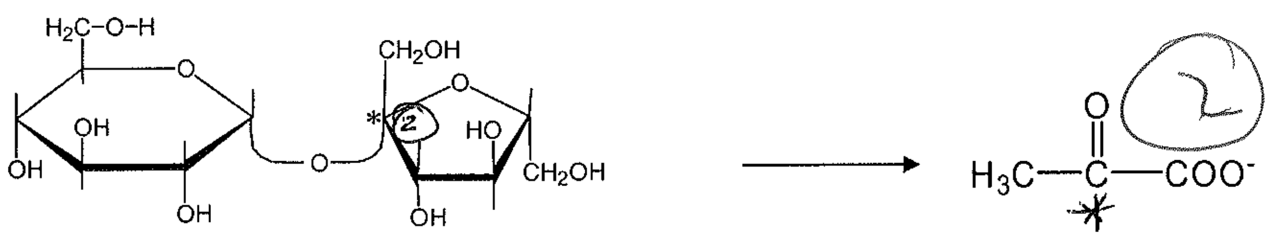
Zero

Question 9 (8 pts). Tracing radiolabels and *etc.* Place asterisks indicating the position of the radiolabel in the molecules shown to the right – if the product contains no radiolabel write "NONE".

a.



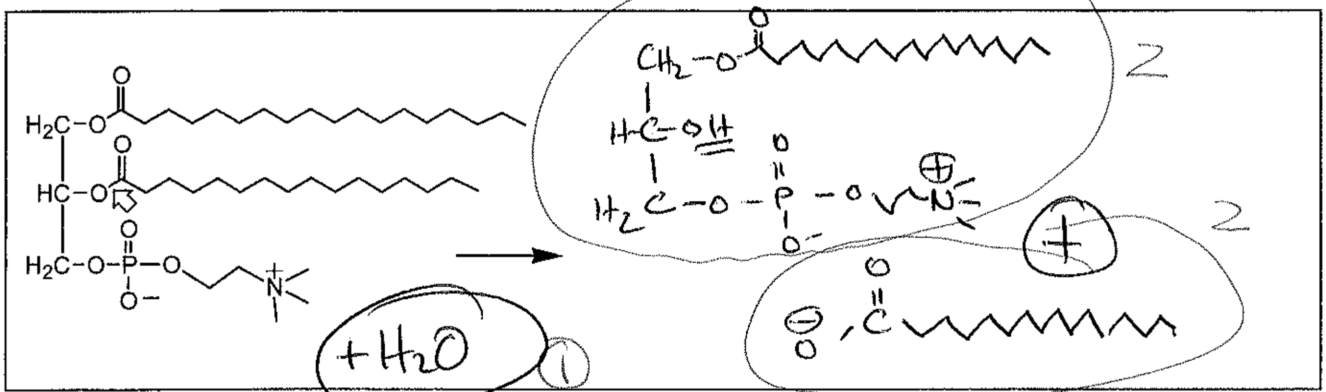
b.



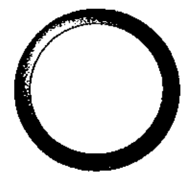
c. In disaccharide "b" number on the structure the carbon marked with an asterisk

d. In disaccharide "b" name the glycosidic linkage α1–2 2

Question 10 (10 pts.). Phospholipase A2 catalyzes the breakdown of molecules like the one shown in the box below by attacking the indicated position. Complete the equation with all other reactants and products of the reaction.



When phospholipase A2 is added to a solution of vesicles (a vesicle is a self-sealed bag of membrane as shown to the right) made up of the substrate shown in the box ... the vesicles remains intact. Explain why only 50% of the substrate is converted to product.



Two lines only: because externally added phospholipase can only

4 hydrolyze outer leaflet & inner & outer leaflets don't equilibrate

If you did FRAP experiments before and after phospholipase treatment what would you expect:

1 one might expect that mobility would be higher (anything reasonable)

Question 11 (4 pts.). The osmotic pressure of 1 mL of a 0.1 M solution of glucose is 2.4 atmospheres (about 36 pound per square inch).

a. Calculate the new osmotic pressure if the same amount of glucose were found in 1 mL of amylose (containing 10,000 glucose units per amylose molecule).

$\frac{2.4}{10,000}$ ATM

= 2.4×10^{-4} **atmospheres**

b. Calculate the new osmotic pressure if the same amount of glucose were found in 1 mL of glycogen (again containing 10,000 glucose units per glycogen molecule).

= 2.4×10^{-4} **atmospheres**

11

K

Question 12 (16 pts.). Fill in the blanks with not more than 3 legible words.

a. name an irreversible inhibitor of an enzyme aspirin

b. and the enzyme that is the target of your answer in "a" cyclooxygenase

(anything reasonable)

c. these enzymes do not follow Michaelis-Menten kinetics allosteric

d. an example of a biological wax beeswax

e. the water-soluble vitamin incorporated into NAD^+ is called NIACIN

f. accumulation of a solute across a biological membrane is called active transport

g. a negative allosteric regulator of glycolysis ATP

h. this process ultimately limits the catalytic efficiency of enzymes DIFFUSION

i. a major regulatory enzyme in glycolysis phosphofructokinase

j. the monosaccharides D-glucose and D-galactose are ___ of one another epimers

k. name a ketotriose dihydroxyacetone

l. a metal frequently associated with kinases magnesium

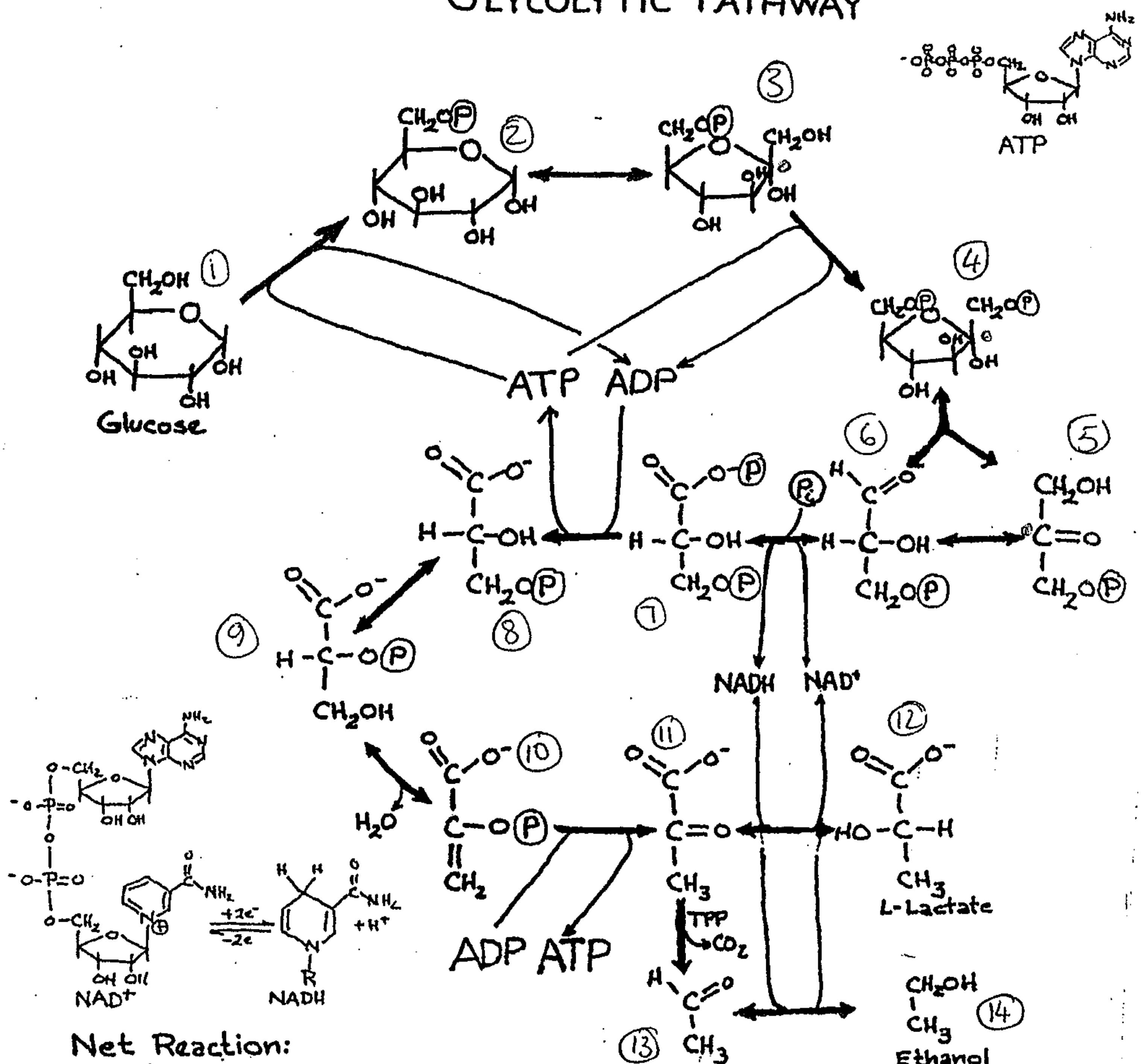
m. a non-saponifiable lipid found in mammalian cell membranes cholesterol

n. a hormone that indirectly activate phosphoryase epinephrine / glucagon

z. how many times have you been taught "glycolysis" X

zz. the word that best describes this exam XXX

GLYCOLYTIC PATHWAY



Net Reaction:

in vertebrates

$$\text{Glucose} + 2P_i + 2\text{ADP} \longrightarrow 2\text{Lactate} + 2\text{ATP}$$

in yeast

$$\text{Glucose} + 2P_i + 2\text{ADP} \longrightarrow 2CO_2 + 2\text{Ethanol} + 2\text{ATP}$$

1/2	hexokinase
2/3	phosphoglucoisomerase
3/4	phosphofructokinase
4/5+6	aldolase
5/6	triosephosphate isomerase
6/7	glyceraldehyde 3P dehydrogenase
7/8	phosphoglycerate kinase
8/9	phosphoglyceromutase
9/10	enolase
10/11	pyruvate kinase
11/12	lactate dehydrogenase
11/13	pyruvate decarboxylase
13/14	alcohol dehydrogenase

HB