# CHEM 527 FIRST EXAM FALL 2002

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 - unfocused, rambling answers won't receive as much credit as a few short appropriate phrases.
6. Please write CLEARLY - if I cannot read it - it is wrong.
7. Good luck

3 ea 2 for correct answer

**Question 1. (21 pts.) Short problems. Show work, but most credit goes to the correct numerical answer.**

a. the pH of a solution is 4.7. What is the hydroxide concentration?

$pH = -\log[H^+]$ $H^+ = 10^{-4.7}$

$[H^+][OH^-] = 10^{-14}$ $OH^- = \frac{10^{-14}}{10^{-4.7}}$

[OH] = $5.01 \times 10^{-10}$ M

$5 \times 10^{-10}$

b. You mix 300 mL of 10 mM KOH with 700 mL of 5 mM HCl. What is the pH of the mixture?

$0.3\,L \times 10\,mmol/L = 3\,mmol$ KOH

$0.7\,L \times 5\,mmol/L = 3.5\,mmol$ HCl

0.5 mmol of HCl remained (in 1L)

pH = 3.3

c. You add 0.5 mmol of formic acid (pK = 3.70) in 250 mL of water to 20 mmol of lithium formate in 250 mL of water. What is the new pH?

$pH = 3.7 + \log \frac{20 \times 10^{-3}}{0.5 \times 10^{-3}}$

$pH = 3.7 + \log(40)$

pH = 5.03

X d. In part "c" .... calculate the pH of the 250 mL of formic acid before the lithium formate was added.

Formic acid $\frac{0.5 \times 10^{-3}\,mol}{0.25\,L} = 2 \times 10^{-3}\,M$ pH = _____

$\frac{[H^+][A^-]}{HA} = \frac{[H^+]^2}{2 \times 10^{-3}} = 10^{-3.7}$ etc.

(IGNORE too dilute to be accurate)

e. A solution of 0.2 moles of lactic acid in 2 L of water showed a pH of 2.4. What is the pK of lactic acid.

0.1 M lactic acid

$H^+ = 10^{-2.4} = .00398\,M$ imeter

So:- (or) $pH = pK + \log \frac{A^-}{HA}$ $2.4 = pK + \log \frac{.00398}{.1}$

$2.4 + 1.4 = pK$

pK = 3.8

f. If you add 0.1 moles of sodium hydroxide to a solution of 0.25 moles of acetic acid (pK=4.7) in 1 L what is the resulting pH?

$pH = 4.7 + \log \frac{0.1\,mol}{.15\,mol}$

pH = 4.52

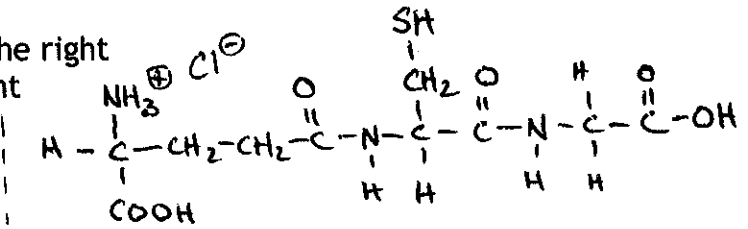
g. Human insulin contains 3 disulfide bonds and no free cysteine side chains. How many possible combinations of disulfide bridged insulin molecules exist?

Number = 15

5 × 3 × 1

(3)

**Question 2. (15 pts)** The molecule shown to the right is called glutathione. It is crucial for antioxidant properties of mammalian cells.



(3) a. What is unusual about its structure? First peptide bond contributed by side chain ... ("iso" peptide bond)

b. Assume pK of 9.5 for the amino group, 8.5 for the -SH group and 3 for the carboxyl groups give the net electrical charge on glutathione at

(3)

pH = 1 +1 (1) pH = 7 −1 (1) pH = 12 −3 (1)

c. You have 0.3 moles of glutathione as shown above. How much KOH needed to get to:

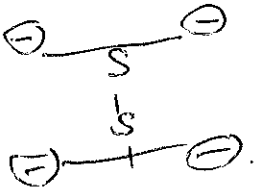
(2)

pH = 8.5 0.75 (1) mol pH=9.5 1.05 (1) mol

d. Two molecules of glutathione can form a **disulfide-linked** dimeric molecule. What is the charge on the dimer at the following pH values:

(2)

pH = 1 +2 (1) pH = 12 −4 (1)



e. Name **and draw** a specific chemical reagent you might use to convert the dimer back to monomers

(2)

(1) β-mercaptoethanol

β-ME

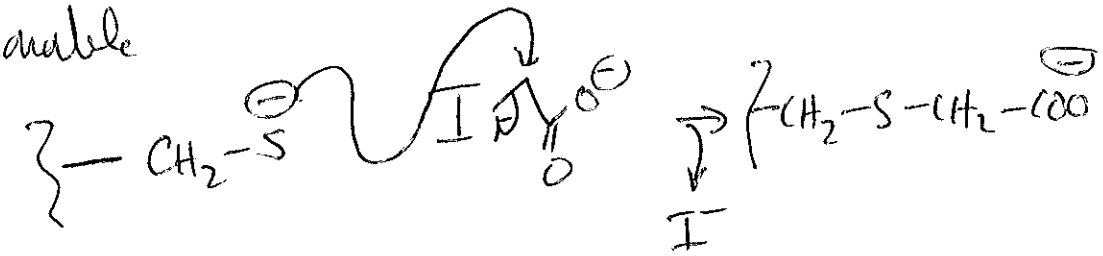
f. What reagent could be used to permanently stop glutathione forming disulfides

iodo acetic acid
iodoacetate

(1)

g. Draw the chemistry involved in your answer in "f":

(2) anything reasonable



**Question 3. (7 pts.) write out the 3 letter amino acid abbreviations for the sequence**

(4)

-MARY- : - MET ALA ARG TYR .

a. What is the chance that the sequence -MARY- would appear in any 4 adjacent amino acid residues in a protein?

(2) $20^4$ $20 \times 20 \times 20 \times 20$

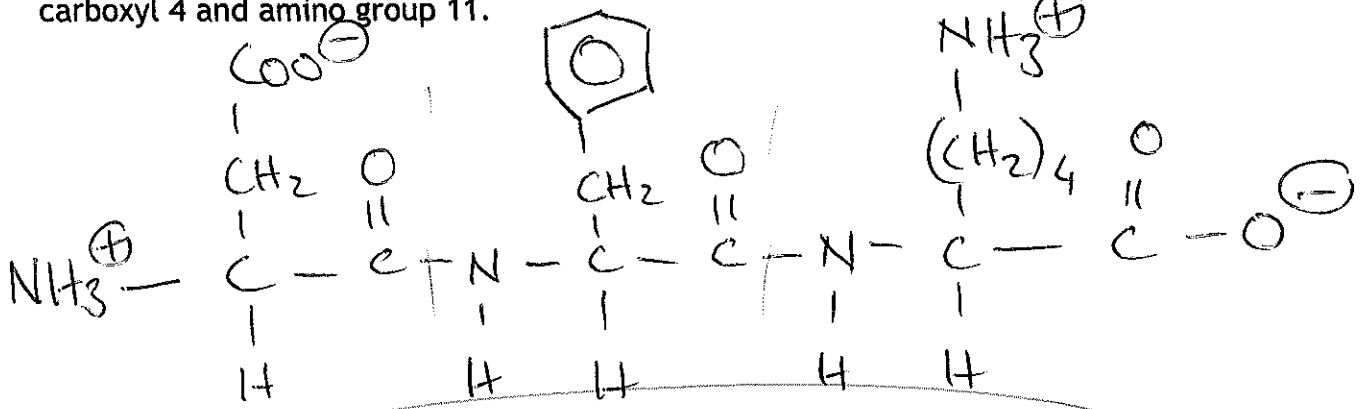
Answer = $\frac{1}{160,000}$

b. If each amino acid had 4 possible pairs of phi/psi angles, how many possible combinations of the 3 dimensional shape of this peptide exist?

(1) $4 \times 4 \times 4 \times 4$

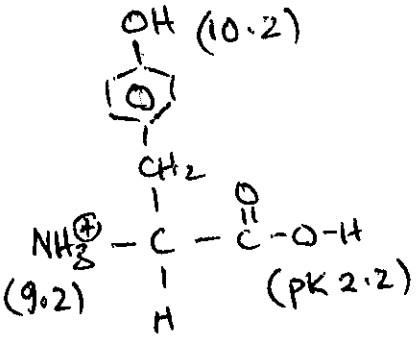
Combinations = 256

**Question 4. (6 pts)** Draw the tripeptide ASP-PHE-LYS in the form that predominates at **pH 5.** Assume the following pK values terminal amino and carboxyl 10 and 2 respectively, side chain carboxyl 4 and amino group 11.

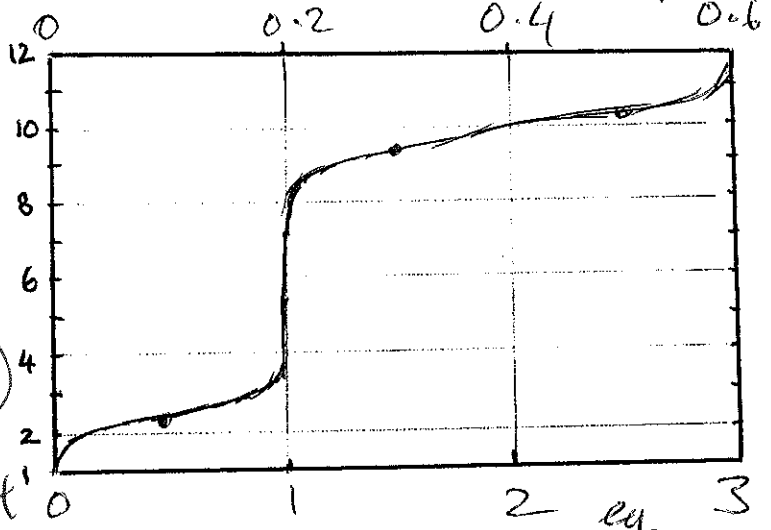


-1 for each, sig fig error

**Question 5. (8 pts)** Tyrosine is shown to the left. At the right draw a clear titration curve of tyrosine. CLARITY and ACCURACY rewarded.




KOH mol



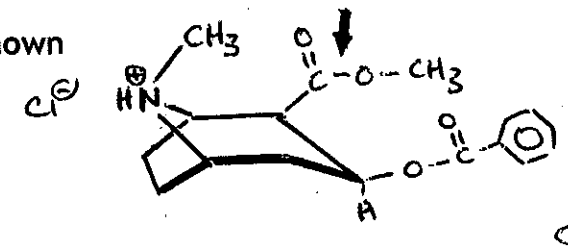

each sig error −1 ±4'

The listed amounts of KOH were added to 0.2 moles of tyrosine in the form shown. Show what pH would result.

0.5 moles 10.2 ; 0.2 moles 5.7 ; 0.1 moles 2.2 ; 0.3 moles 9.2

KOH

**Question 6. (7 pts.) Cocaine hydrochloride is shown to the right and has a pK of 5.6. Cocaine is dissolved in buffers of pH 3, 5 and 8.**




Which would provide the faster absorption into a biological membrane? pH = 8 (2)

Which pH (3, 5 or 8) would you expect cocaine to be most soluble? pH = 3 (1)

What happens to the pK of the amino group if cocaine goes from water into a hydrophobic solvent? Circle one answer:

It remains the same  it increases  (it decreases)  cannot predict  (1)

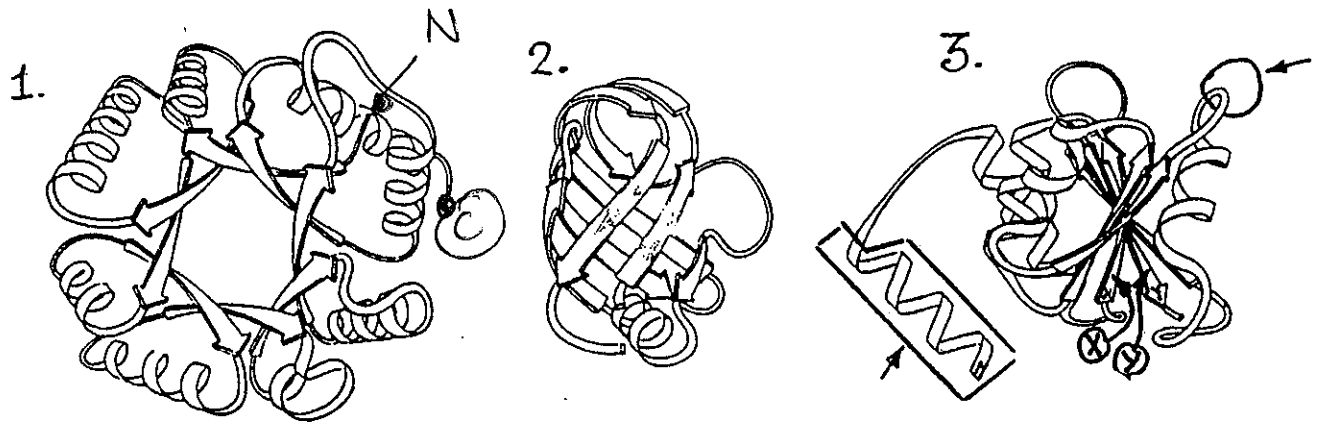
Hydrolysis of the ester linkage shown by the arrow in the diagram generates an acid derivative with a pK of 3.0. The new rate of absorption of the derivative would be __ than cocaine at the same pH:

At pH = 3: faster (slower) unchanged (circle) (1)

At pH = 5: faster (slower) unchanged (1)

At pH = 8: faster (slower) unchanged (1)

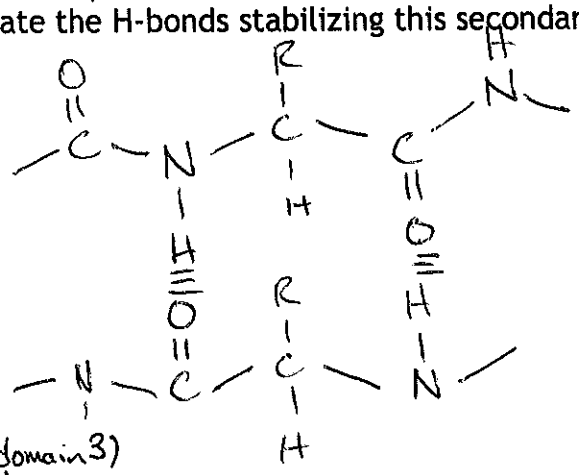
**Question 7. (14 pts) the following domains are found in the enzyme pyruvate kinase:**




(2) a. In domain 1 - clearly label the N and C termini.

b. In domain 3 - draw a short stretch of the two adjacent polypeptide chains labeled X and Y. Use R-to represent the side chains, but otherwise include all atoms in your drawing. Clearly indicate the H-bonds stabilizing this secondary structure.

(4)




(2) X and Y are part of what type of structure? β-Structure

(2) How many amino acids would you expect in the boxed in area of domain 3 (3×3.6) Number: 10 ~ 12 (10.8)

(1) Which amino acid would you least expect in the middle of this section PRO / or GLY

Name the structural element circled in domain 3 TURN

Domain 2 has many lysine and arginine residues - but it is not attacked by trypsin treatment. Suggest a reason why.

(2) WELL FOLDED to prevent Trypsin from accessing — (ARG/LYS) ↓ x —

**Question 8. (7 pts.) From the following 8 peptides (A-H) select a single letter for each question. You may use letters more than once.**

A TRP-LEU-LYS  B LYS-THR-GLY  C GLU-CYS-MET  D GLU-ASP-ARG

E ALA-LYS-ARG  F PHE-THR-GLU  G PHE-ARG-PRO  H MET-PHE-LEU

Which peptide has the largest absorbance at 280 nm A

Which peptide is the most positively charged at pH 6 E

Which peptide has approximately no charge at pH 6 H

Which peptide could be fragmented by CNBr (cyanogen bromide) H

A peptide resistant to trypsin and chymotrypsisn C or D

The most polar peptide at pH 7 D

This peptide tends to dimerize on standing C

**Question 9. (6 pts) Using the table, answer the following. None of the protein contained disulfide bonds**

| Protein | overall molecular weight | pI | # subunits |
|---|---|---|---|
| A | 45,000 | 4 | 2 |
| B | 90,000 | 3 | 1 |
| C | 15,000 | 9 | 1 |
| D | 160,000 | 7 | 4 |

a. the protein sticking tightest to a positively charged resin at pH 8 B

b. the protein sticking tightest to a negatively charged resin at pH 7 C

c. The protein running slowest on SDS-PAGE B

d. The protein with the largest proportion of (ASP + GLU) compared to (LYS + ARG) B

e. The protein that emerges slowest on gel filtration C

f. The protein that comes out first on gel filtration D

**Question 10 (pts.) Fill in the blanks with not more than 3 legible words.**

a. these catalysts aid folding of large proteins — FOLDASES / chaperones

b. the amino acid obligatorily present at every 3rd position in collagen — GLY

c. A shell of ordered water around an organic molecule is called — CLATHRATE

d. Plots of the frequency of phi/psi angles in proteins are called — RAMACHANDRAN PLOT

e. An example of a protein toxin — BOTULINUM / RICIN

f. A vitamin required for collagen maturation — VIT C / ASCORBIC

g. A method for determining 3D structure without crystals — NMR

h. The name of the most commonly used protein sequencing method — EDMAN

zz. the word that best describes this exam — ODE

the end