BCH 4053 **HOUR TEST 1** **NAME______KEY________**
January 31, 2001

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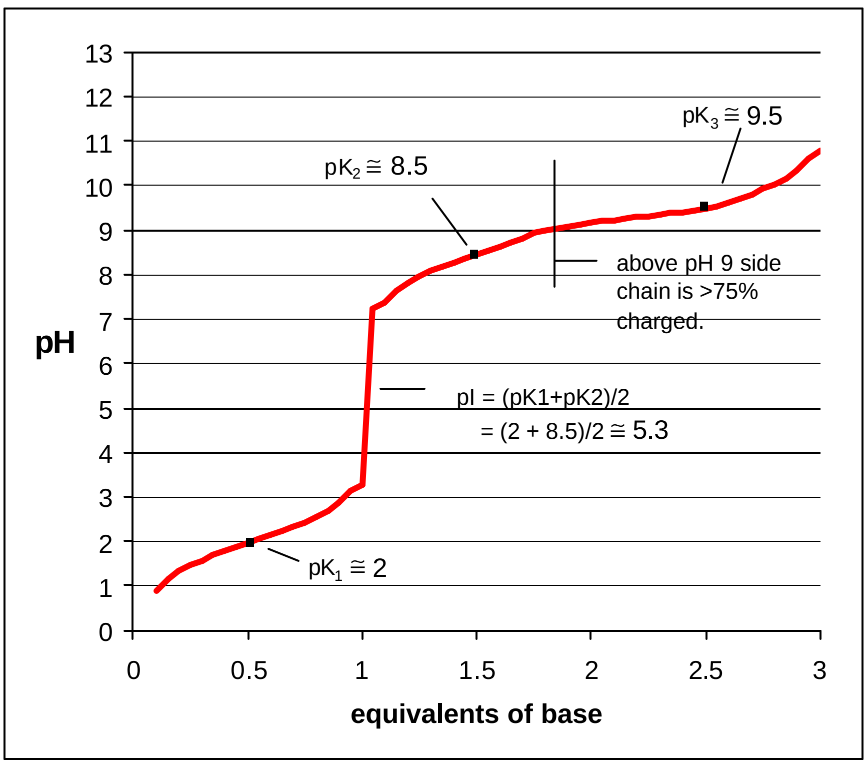
(10) 1. Vitamin C (ascorbic acid) is a diprotic acid, with dissociation constants: $pK_1 = 4.1$; $pK_2 = 11.8$. If vitamin C were excreted in the urine of a patient, and the urine had a pH of 4.5, what **fraction** of the vitamin would carry a negative charge? (Note: I am asking for a **fraction** and not a **ratio**). 5 pts ratio, 5 pts fraction, accept 72%

$$AsH_2 \xrightarrow[4.1]{pK_1} AsH^- \xrightarrow[11.8]{pK_2} As^{2-} \quad (\text{need consider only } pK_1)$$

$$\frac{[AsH^-]}{[AsH_2]} = 10^{pH-pK} = 10^{4.5-4.1} = 10^{0.40} = 2.51$$

$$\text{fraction of } AsH^- = \frac{[AsH^-]}{[AsH]+[AsH^-]} = \frac{2.51}{1+2.51} = \frac{2.51}{3.51} = 0.72$$

(14) 2. Draw a titration curve for **cysteine** on the graph below.
(a) Locate and identify the points on the curve corresponding to $\mathbf{pK_1}$, $\mathbf{pK_2}$, and $\mathbf{pK_3}$.
(b) Calculate the approximate **pI** value and locate its position on the curve.
(c) Indicate the pH region of the graph in which the **side chain functional group** is more than 75% charged.



2 pts ea: pK_1, pK_2, pK_3; 3 pts ea. pI, pH of 75% side chain charge, 2 pts shape and location of curve

(9) 3. **Underline** the following peptides which are negatively charged at pH 7.0. **Circle** each amino acid which is **aromatic**. Put an **X** through each amino acid that contains a **sulfur atom**.

1 pt ea. Correctly underlined or not; 1 pt each circled, 1 pt each X, -0.5 for incorrect circling or X.

gln.phe.tyr.ala (pI = (3+8)/2 = 5.5) his.arg.gly.trp (pI = (8+12)/2 = 10)

ile.lys.met.asp (pI = (4+8)/2 = 6) cys.pro.glu.asn (pI = (3+4)/2 = 3.5)

(12) 4. Fill in the following table with the appropriate $[H^+]$, pH, and $[OH^-]$ values:

1 pt each answer. OK if more sig. fig's.

Solution	**$[H^+]$**	**pH**	**$[OH^-]$**
2.1×10^{-3} HCl	2.1×10^{-3} M	2.7	4.8×10^{-12} M
4.9×10^{-5} NaOH	2.0×10^{-10} M	9.7	4.9×10^{-5}
3.6×10^{-9} HBr	10^{-7} M	7.0	10^{-7} M
0.05 M acetic acid ($pK_a = 4.8$)	*8.9×10^{-4} M	3.1 (or 3.0)	1.1×10^{-11} M

$$^*[H^+] \cong \sqrt{K_a c} = \sqrt{(10^{-4.8})(0.05)} = 8.9 x 10^{-4}$$

(12) 5. You have a solution of 500 mL of 0.24 M formate buffer with a pH of 4.45. **The pK of formic acid is 3.75.** To this solution you add 40.0 mL of 1.0 M hydrochloric acid. What is the final pH of the solution? (Show your work).

Find the amount of each protonated form to start:

$$n\,formate = 500\,mL\,x\,\frac{0.24\,mmol}{mL} = 120\,mmol = n\,HCOOH + n\,HCOO^-$$

$$\frac{[HCOO^-]}{[HCOOH]} = \frac{nHCOO^-}{n\,HCOOH} = 10^{pH-pK} = 10^{4.45-3.75} = 10^{0.70} = 5.0$$

$$n\,HCOOH + (5.0)nHCOOH = 120\,mmol$$

$$n\,HCOOH = \frac{120\,mmol}{1+5} = 20\,mmol$$

$$n\,HCOO^- = (5.0)(20\,mmol) = 100\,mmol \quad (check:\ 20\,mmol + 100\,mmol = 120\,mmol)$$

Then add the acid:

$$n\,H^+ = 40\,mL\,x\,\frac{1\,mmol}{mL} = 40\,mmol$$

	$HCOO^-$	+ H^+	$\rightarrow HCOOH$
initial	100mmol	40mmol	20mmol
change	− 40mmol	− 40mmol	+ 40mmol
equil.	60mmol	~ 0	60mmol

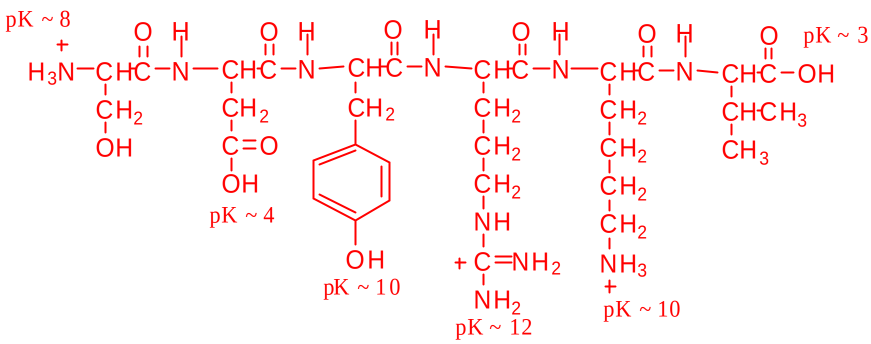
$$final\,pH = pK + \log\frac{[nHCOO^-/vol]}{[nHCOOH/vol]} = 3.75 + \log\frac{[60\,mmol/\cancel{vol}]}{[60\,mmol/\cancel{vol}]} = 3.75 + 0 =$$

2 pts each: quantity of HCOOH and $HCOO^-$ at beginning, at end, quantity of acid, and calculation of final pH

(7) 6. Draw the full structure of the following peptide and indicate on the structure the pK of each group with a dissociable proton. Calculate the pI of the peptide.

0.5 pts each structure (stick figures ok); 0.5 pts pK (+/- 0.5 units), 1 pt pI (+/- 0.5 units)

ser.asp.tyr.arg.lys.val



$p^{3+} \rightarrow p^{2+} \rightarrow p^{+} \rightarrow p^{0} \rightarrow p^{1-} \rightarrow p^{2-} \rightarrow p^{3-}$

pK_1~3 pK_2~4 pK_3~8 pK_4~10 pK_5~10 pK_6~12

pI ~ $(pK_3+pK_4)/2$ = (~8+~10)/2 = ~9

(4) 7. Peptide A has a pI of 9.5. Peptide B has a pI of 6.0. Put a check by each of the following statements which is true.

0.5 pts each blank correctly checked or left unchecked.

____ Both peptides will bind to an anion exchange resin at pH 7.

____ Both peptides will bind to a cation exchange resin at pH 7.

_X__ Peptide A will bind to a cation exchange resin at pH 7.

____ Peptide B will bind to a cation exchange resin at pH 7.

____ Peptide A will bind to an anion exchange resin at pH 7.

_X__ Peptide B will bind to an anion exchange resin at pH 7.

____ Both peptides will bind to an anion exchange resin at pH 4.

_X__ Both peptides will bind to a cation exchange resin at pH 4.

(6) 8. In the hydrophobic effect, the association of non-polar groups in water is spontaneous. Therefore ΔG for the process is _negative__ (negative or positive?). The association occurs primarily because the water is more disordered in the state where the non-polar groups are associated. Therefore the overall ΔS for the process is _positive__ (negative or positive?). Lowering the temperature in this case would _decrease____ (increase or decrease) the strength of the hydrophobic bonding? (Hint: How would ΔG be affected?)

2 pts each blank. (lowering T makes the -TΔS term less negative, hence ΔG less negative)

(8) 9. What are the "biological standard states" for:

(a) water? Pure water

(b) oxygen? Oxygen at 1 atmosphere pressure

(c) hydrogen ion? $[H^+] = 10^{-7}$ M

(d) ATP? [ATP] = 1 M

Use the following standard free energies of hydrolysis to answer questions 10 and 11.

Compound	**D$G^{o\prime}$ (kJ/mol)**	**Compound**	**D$G^{o\prime}$ (kJ/mol)**
phosphoenolpyruvate	-62.2	glucose-1-phosphate	-21.0
acetyl phosphate	-43.3	glucose-6-phosphate	-13.9
ATP	-30.5	glycerol-3-phosphate	-9.2
Creatine phosphate	-43.3	Pyrophosphate	-33.6

(12) 10. One of the reactions of glycolysis producing ATP is the reaction of ADP with phosphoenolpyruvate as follows:

phosphoenolpyruvate + ADP ⇄ pyruvate + ATP

(a) Calculate D$G^{o\prime}$ and **K'** for this reaction as written. (**R = 8.315 J/mol-K. Assume body temperature --37 °C or 310 K**)

$$\Delta G^{o\prime} = \Delta G^{o\prime}_{PEPhydrolysis} - \Delta G^{o\prime}_{ATPhydrolysis} = -62.2\frac{kJ}{mol} + 30.5\frac{kJ}{mol} = -31.7$$

$$K' = e^{-\frac{\Delta G^{o\prime}}{RT}} = e^{-\frac{-31.7\frac{kJ}{mol}}{(8.315\frac{J}{mol-K})(\frac{1kJ}{10^3 J})(310K)}} = e^{12.3} = 2.19x10^5$$

2 pts ΔG calculation, 2 pts set-up for K', 2 pts. K' calculation.

(b) What would **Q'** and D**G** be for the reaction if the [ATP]/[ADP] ratio were 50 and the [phosphoenolpyruvate]/[pyruvate] ratio were 0.010?

$$Q' = \frac{[pyruvate][ATP]}{[phosphoenolpyruvate][ADP]} = \frac{[1][50]}{[0.010][1]} = 5x10^3$$

$$\Delta G = \Delta G^{o\prime} + RT\ln Q = -31.7\frac{kJ}{mol} + (8.315x10^{-3}\frac{kJ}{mol-K})(310K)\ln(5x10^3)$$

$$= (-31.7 + 2\not{1}.\not{9}\not{5}\ 2.0)\frac{kJ}{mol} = -9.7\ \frac{kJ}{mol}$$

2 pts Q' calculation, 2 pts setup for ΔG, 2 pts ΔG calculation

(6) 11. Tell whether each of the following reactions is **spontaneous** or **non-spontaneous** as written.

spontaneous_ (a) glucose + acetyl-phosphate ⇄ glucose-6-phosphate + acetate

non-spontan. (b) glucose-6-phosphate ⇄ glucose-1-phosphate

spontaneous_ (c) creatine phosphate + ADP ⇄ creatine + ATP