CHEM 3530 - Exam 4 – April 21, 2017

Name Solutions

(76) **PART I. MULTIPLE CHOICE (Circle the ONE correct answer)**

For #1 - #4: Consider.the base, aniline (Anil), which has a base equilibrium constant, $K_b = 4.3 \times 10^{-10}$.

1. What is the pH of a 0.05 Molar aqueous solution of aniline (Anil)?

   (A) 3.0 (B) 5.3 (C) 8.7 (D) 11.0

2. What is the pH of a 0.05 Molar aqueous solution of anilinium chloride (AnilHCl)?

   (A) 3.0 (B) 5.3 (C) 8.7 (D) 11.0

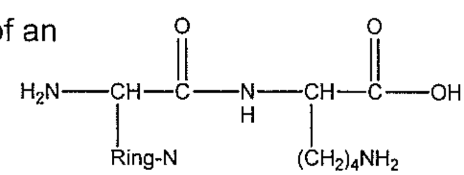
3. What is the pH after 0.3 moles of HCl is added to 3 Liters of 0.40 Molar aqeuous aniline?

   (A) 4.1 (B) 9.8 (C) 8.9 (D) 5.1

4. What is the ratio, $[AnilH^+]/[Anil]$ at pH = 4.2 ($AnilH^+$ is the conjugate acid]?

   (A) 2.7 (B) 0.74 (C) 0.37 (D) 8.6

For #5 - #9: consider the dipeptide (Pep) consisting of an Histidine residue and a Lysine residue (the neutral form is pictured on right)
Note: The most positive, low pH, form of this dispeptide has a charge = +3



The two side groups ionize according to:

$-Ring\text{-}NH^+ \rightarrow H^+ + -Ring\text{-}N$ and $-(CH_2)_4NH_3^+ \rightarrow H^+ + -(CH_2)_4NH_2$

The four pK_a's are: pK_a' (α-CO_2H) = 2.2, pK_a''(Ring-NH^+) = 6.0, pK_a'''(α-NH_3^+) = 9.8, and pK_a''''(ε-NH_3^+) = 10.6

5. What is the pH after 1.5 equivalents of NaOH are added to a solution containing the most acidic form of Pep?

   (A) 2.2 (B) 4.1 (C) 6.0 (D) 7.9

6. What is the pH after 250 mL of 1.6 M NaOH are added to 200 mL of 0.80 M Pep in the most acidic form?

(A) 4.1 (B) 6.0 (C) 7.9 (D) 9.8

7. What pH corresponds to the isoelectric point, pI, of Pep?

(A) 7.9 (B) 9.8 (C) 10.2 (D) 10.6

8. What is the average charge of Pep at pH = 7.9?

(A) +1.0 (B) +0.5 (C) -0.5 (D) -1.0

9. What species are present in a Pep solution buffered to pH = 5.0?

(A) Pep^{3+} & Pep^{2+} (B) Pep^{2+} & Pep^{1+} (C) Pep^{1+} and Pep^{0} (D) Pep^{0} and Pep^{1-}

10. Three proteins, A, B, and C, have the same Molar Mass and size, but different isoelectric points, pI(A)= 4.5 , pI(B)= 7.5 , pI(C)= 10.0. If they if they are put onto an electrophoresis column buffered at pH=6.0, then

(A) A, B and C will migrate towards the positive electrode
(B) A, B and C will migrate towards the negative electrode
(C) A will migrate towards the negative electrode, B and C towards the positive electrode
(D) A will migrate towards the positive electrode, B and C towards the negative electrode

11. In class, we discussed the buffering action of the CO_2/HCO_3^- and Hemoglobin (Hb) buffers in controlling the pH in blood? Which of the following statements is/are true?

(i) Because the principal metabolism products are carboxylic acids, the large excess of HCO_3^- relative to CO_2 makes this a suitable buffer to remove the added acid.

(ii) CO_2 produced in the muscles lowers the pH of the blood, which is then raised by the Hb buffer.

(iii) The Hb molecules in muscles become more saturated with O_2 at lower pH's

(A) i only (B) i and ii (C) i and ii and iii (D) ii and iv

For #12 - #13: consider the slightly soluble compound, Ag_2CO_3, which dissociates which dissolves in water according to the equation, $Ag_2CO_3(s) = 2Ag^+(aq)+CO_3^-(aq)$. The solubility product (aka solubility constant) is $K_S= 6.2x10^{-12}$.

12. What is the solubility of Ag_2CO_3 in pure water?

(A) $1.2x10^{-4}$ M (B) $1.8x10^{-4}$ M (C) $1.2x10^{-6}$ M (D) $2.5x10^{-6}$ M

13. What is the concentration of silver ions, $[Ag^+]$, in a solution containing Ag_2CO_3 and 0.1 M $K_2CO_3(aq)$?

(A) 1.6×10^{-5} M (B) 7.9×10^{-6} M (C) 3.9×10^{-6} M (D) 2.5×10^{-6} M

14. The reaction, A → P, is of order "x". A plot of $1/[A]^3$ vs. t is a straight line. The order of the reaction, x, is

(A) -2 (B) 3 (C) 2 (D) 4

For #15 - #16: Consider a reaction, A → Products, which is of order "n"; i.e. Rate = $k[A]^n$. For this reaction, the following initial rate data was obtained.

When $[A]_o$ = 0.15 M, the initial rate is 6.80 M/min

When $[A]_o$ = 0.60 M, the initial rate is 1.70 M/min

15. The order of this reaction (i.e. "n") is:

(A) -2 (B) -1 (C) +1 (D) +2

16. The rate constant for this reaction (i.e. "k") is approximately:

(A) 6.3 $M^2\ min^{-1}$ (B) 0.15 $M^3\ min^{-1}$ (C) 1.0 $M^2\ min^{-1}$ (D) 45 min^{-1}

17. Consider the reaction, A →P, which is **second** order; i.e. r = $k[A]^2$. The rate constant for this reaction is 0.02 $M^{-1}s^{-1}$. When $[A]_0$ = 0.80 M, then 100 s after the start of the reaction, the concentration, [A], will be approximately

(A) 0.31 M (B) 0.14 M (C) 0.42 M (D) 0.11 M

18. Thallium-201 is a radioisotope which is used for myocardial imaging tests. Its half-life is 73 hours (which corresponds to a rate constant of $9.5 \times 10^{-3}\ hrs^{-1}$). Approximately how long will it take for the amount of Thallium-201 in the body to be reduced to 10% of its initial amount upon injection?

(A) 190 hrs. (B) 240 hrs. (C) 270 hrs. (D) 290 hrs.

19. The half-life for the nuclear transformation of ^{40}K to ^{40}Ar is 1.25 billion years. If a rock was formed 3.2 billion years ago, then the ratio of the two elements, $[^{40}Ar]/[^{40}K]$, is approximately:

(A) 0.2 (B) 2.7 (C) 4.9 (D) 8.6

PART II. TWO (2) PROBLEMS FOLLOW (Show work for partial credit)

$Leu^+ \rightleftharpoons Leu \rightleftharpoons Leu^-$
2,3 9.7

(12) 1. Leucine (Leu) is an amino acid with R= $-CH_2CH(CH_3)_2$. Its pK_a's are: $pK_a'(\alpha-CO_2H)$= 2.3 and $pK_a''(\alpha-NH_3^+)$= 9.7.

If one prepares a 0.8 Molar solution neutral leucine and raises the pH to 10.3, what are the concentrations, [Leu] and [Leu^{-1}], in the resulting solution?

$$pH = pK_a'' + \log \frac{[Leu^-]}{[Leu]} \rightarrow 10.3 = 9.7 + \log \frac{[Leu^-]}{[Leu]}$$

$$\log \frac{[Leu^-]}{[Leu]} = 10.3 - 9.7 = 0.60 \qquad \frac{[Leu^-]}{[Leu]} = 10^{0.6} = 3.98$$

$$[Leu^-] = 3.98[Leu]$$

$$[Leu] + [Leu^-] = 0.80M$$

$$[Leu] + 3.98[Leu] = 0.8 = 4.98[Leu]$$

$$[Leu] = \frac{0.8}{4.98} = \boxed{0.16\ M}$$

$$[Leu^-] = 0.80 - 0.16 = \boxed{0.64M}$$

(12) 2. Consider the reaction, A → Products, which is of order 3/2; i.e. Rate = $k[A]^{3/2}$. The integrated rate equation for a 3/2 order reaction is:

$$\frac{1}{[A]^{1/2}} - \frac{1}{[A_0]^{1/2}} = \frac{1}{2}kt$$

For a given 3/2 order reaction, the initial concentration, $[A]_0$, is 0.60 M, and the rate constant, k, is 0.010 $M^{-1/2}\ s^{-1}$.

(6) (a) How long from the start of the reaction would it take for the concentraton of A to decrease from 0.60 M to 0.40 M ?

$$t = \frac{2}{k}\left(\frac{1}{[A]^{1/2}} - \frac{1}{[A]_0^{1/2}}\right) = \frac{2}{0.01\,M^{-1/2}s^{-1}}\left[\frac{1}{(0.4M)^{1/2}} - \frac{1}{(0.6M)^{1/2}}\right]$$

$$= \boxed{58\ s}$$

(6) (b) What will be the concentration, [A], 120 seconds after the start of the reaction ?

$$\frac{1}{[A]^{1/2}} = \frac{1}{[A]_0^{1/2}} + \frac{1}{2}kt = \frac{1}{(0.6M)^{1/2}} + \frac{1}{2}(0.01\,M^{-1/2}s^{-1})(120s)$$

$$\frac{1}{[A]^{1/2}} = 1.89\,M^{-1/2}$$

$$[A]^{1/2} = \frac{1}{1.89\,M^{-1/2}} = 0.53\,M^{1/2}$$

$$[A] = (0.53\,M^{1/2})^2 = \boxed{0.28\,M}$$