CHEM 3530 - Exam 4 – April 20, 2018

Name Solutions

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

For #1 - #4: Consider hypobromous acid (HBrO), which has an acid dissociation constant, $K_a = 2.0 \times 10^{-9}$.

1. What is the pH of a 0.20 M solution of aqueous hypobromous acid (HBrO)?

   (A) 3.0 (B) 4.7 (C) 9.3 (D) 11.0

2. What is the pH of a 0.20 M solution of aqueous potassium bromite (KBrO)?

   (A) 3.0 (B) 4.7 (C) 9.3 (D) 11.0

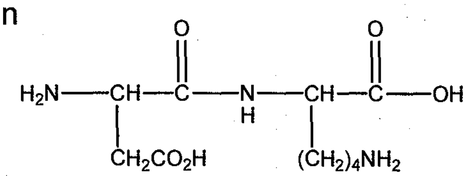
3. What is the pH of a solution after 0.50 L of 0.40 M HCl are added to a 2 L solution of a 0.40 M solution of potassium bromite?

   (A) 8.2 (B) 4.8 (C) 9.2 (D) 5.8

4. What is the value of the ratio, $[HBrO]/[BrO^-]$ at pH = 9.1:

   (A) 0.40 (B) 0.67 (C) 1.50 (D) 2.50

For #5 - #9, consider the dipeptide (Pep) consisting of an Aspartic Acid residue and a Lysine residue (pictured on right)
Note: The most positive, low pH, form of this dispeptide has a charge = +2



The two side groups ionize according to:
$-CH_2CO_2H \rightleftharpoons H^+ + -CH_2CO_2^-$ and $-(CH_2)_4NH_3^+ \rightleftharpoons H^+ + -(CH_2)_4NH_2$

The four pKa's are: pK_a' (α-CO_2H) = 2.1, pK_a''(β-CO_2H) = 3.9, pK_a'''(α-NH_3^+) = 9.9, and pK_a''''(ε-NH_3^+) = 10.5

5. What is the pH after 3.5 equivalents of NaOH are added to the most acidic form of pep?

   (A) 6.9 (B) 9.9 (C) 10.2 (D) 10.5

6. How many equivalents of NaOH must be added to the most acidic form of Pep to reach the isoelectric point, pI?

   (A) 1.0 (B) 2.0 (C) 3.0 (D) 3.5

7. What is the pH after 100 mL of 1.5 M NaOH are added to 200 mL of 0.30 M Pep in the most acidic form?

(A) 3.0 (B) 3.9 (C) 6.9 (D) 9.9

8. What is the average charge of Pep at pH = 9.9?

(A) -1.5 (B) -1.0 (C) -0.5 (D) -2.0

9. What species has the highest concentration at pH = 8.5?

(A) pep^{+1} (B) pep (C) pep^{-1} (D) pep^{-2}

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=9.0, 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 & B will migrate towards the negative electrode, and C towards the positive electrode
(D) A & B will migrate towards the positive electrode, 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?

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

X (ii) CO_2 produced in the muscles raises the pH of the blood, which is then lowered by the Hb buffer.

✓ (iii) The Hb molecules in blood transport the CO_2 produced by exercise from the muscles to the lungs.

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

12. The reaction A → Products, is of order 3/2; i.e. rate=$k[A]^{3/2}$. Which plot will give a straight line?

(A) $1/[A]^{3/2}$ vs. t (B) $1/[A]^{1/2}$ vs. t (C) $1/[A]^{5/2}$ vs. t (C) $[A]^{1/2}$ vs. t

13. The reaction, A → Products, is third order. When the initial concentration, $[A]_o$=0.05 M, the initial rate is r_o= 0.15 M/s. Therefore, the rate constant, k, is

(A) $1.2\times10^3\ M^{-2}s^{-1}$ (B) $3.33\ M^{-2}s^{-1}$ (C) $1.9\times10^{-5}\ M^{-2}s^{-1}$ (D) $8.3\times10^{-4}\ M^{-2}s^{-1}$

14. The reaction, A → P, is of order "x"; i.e. rate = $k[A]^x$. When $[A_o]$= 0.3 M, the half-life of the reaction is 200 s. When $[A]_o$= 0.6 M, the half life of the reaction is 50 s. The order of the reaction, x, is

(A) -1 (B) 1 (C) 2 (D) 3

15. Consider the reaction, $A \rightarrow P$, which is **second** order; i.e. $r = k[A]^2$. When the initial concentration is $[A]_0 = 0.6$ M, it takes 150 seconds for the concentration, [A], to decrease to 0.2 M. Therefore, the rate constant for this reaction is:

(A) $2.2 \times 10^{-2}\ M^{-1}s^{-1}$ (B) $1.1 \times 10^{-2}\ M^{-1}s^{-1}$ (C) $7.3 \times 10^{-3}\ M^{-1}s^{-1}$ (D) $5.0 \times 10^{2}\ M^{-1}s^{-1}$

16. The half-life of ^{14}C is $t_{1/2} = 5730$ yr. (corresponding to $k = 1.21 \times 10^{-4}\ yr^{-1}$). The natural abundance of ^{14}C in living matter is 1×10^{-12} mol %. If an artifact is 14,000 years old, what will be the natural abundance of ^{14}C in the artifact?

(A) 1.8×10^{-13} mol % (B) 2.7×10^{-13} mol % (C) 5.6×10^{-13} mol % (D) 1.1×10^{-13} mol %

17. The half-life for the nuclear transformation of ^{40}K to ^{40}Ar is 1.25 billion years. In a given rock, the ratio of ^{40}K to ^{40}Ar is: $[^{40}K]/[^{40}Ar] = 0.70$. The age of this rock is:

(A) 2.7 billion yrs. (B) 0.9 billion yrs. (C) 1.6 billion yrs. (D) 0.4 billion yrs

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PART II. THREE (3) PROBLEMS FOLLOW (Show work for partial credit)

(10) 1. HCN is a weak acid with $K_a = 4.9 \times 10^{-10}$. A solution of 0.60 M KCN is prepared and the pH is adjusted to 9.00. Calculate the concentrations, [HCN] and $[CN^{-1}]$ of the solution.

$$pK_a = -\log(4.9 \times 10^{-10}) = 9.31$$

$$pH = pK_a + \log \frac{[CN^-]}{[HCN]}$$

$$9.00 = 9.31 + \log \frac{[CN^-]}{[HCN]}$$

$$\log \frac{[CN^-]}{[HCN]} = 9.00 - 9.31 = -0.31 \qquad \frac{[CN^-]}{[HCN]} = 10^{-0.31} = 0.49$$

$$\text{or } [CN^-] = 0.49[HCN]$$

$$[HCN] + [CN^-] = 0.60$$

$$[HCN] + 0.49[HCN] = 0.60$$

$$1.49[HCN] = 0.60$$

$$[HCN] = \frac{0.60}{1.49} = 0.40\ M$$

$$[CN^-] = 0.6 - [HCN] = 0.60 - 0.40 = 0.20\ M$$

$$H_2SeO_3 \underset{2.46}{\rightleftharpoons} HSeO_3^- \underset{7.30}{\rightleftharpoons} SeO_3^{2-}$$

(10) 2. Selenous Acid, H_2SeO_3, is a diprotic acid with pKa's:
pKa' = 2.46 , pKa" = 7.30

$V = 1500 mL = 1.5 L$

Calculate the pH of a solution prepared by adding 700 mL of 1.00 M HCl to 800 mL of 0.50 M sodium selenite, Na_2SeO_3.

Init: $n_{SeO_3^{2-}} = 0.5 mol/L \times 0.8 L = 0.40 mol$.

$n_{H^+} = 1.0 mol/L \times 0.7 L = 0.70 mol$.

Because we have more than 1 equiv. of H^+, this is a two step neutral.

Step 1

	SeO_3^{2-}	$+ H^+$	$\rightarrow HSeO_3^-$
init	0.40	0.70	0
chg	−0.40	−0.40	+0.40
	0	0.30 mol	0.40 mol

Step 2

	$HSeO_3^-$	$+ H^+$	$\rightarrow H_2SeO_3$
init	0.40	0.30	0
chg.	−0.30	−0.30	+0.30
	0.10 mol		0.30 mol

← not actually necessary

$[HSeO_3^-] = \frac{0.10 mol}{1.5 L} = 0.067 M$ $[H_2SeO_3] = \frac{0.30 mol}{1.5 L} = 0.20 M$

$pH = pK_a' + \log \frac{[HSeO_3^-]}{[H_2SeO_3]} = 2.46 + \log\left(\frac{0.067}{0.20}\right)$

$= 2.46 - 0.48 = \boxed{1.98}$

↑ you can use moles and get same answer.

3.

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

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt$$

For a given third order reaction, the initial concentration is $[A]_0 = 0.80$ M, and the rate constant is k= 0.10 $M^{-2}s^{-1}$.

(6) (a) How long from the start of the reaction would it take for the concentraton of A to decrease from 0.80 M to 0.30 M ?

$[A_0] = 0.80 M$
$[A] = 0.30 M$
$k = 0.10 M^{-2}s^{-1}$

$$t = \frac{1}{2k}\left[\frac{1}{[A]^2} - \frac{1}{[A_0]^2}\right] = \frac{1}{2(0.1 M^{-2}s^{-1})}\left[\frac{1}{(0.30M)^2} - \frac{1}{(0.80M)^2}\right]$$

$= 47.7 s \approx$ **48 s**

(6) (b) What will be the concentration, [A], 140 seconds after the start of the reaction ?

$[A_0] = 0.80 M$
$k = 0.1 M^{-2}s^{-1}$
$t = 140 s$

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

$$= \frac{1}{(0.8M)^2} + 2(0.1 M^{-2}s^{-1})(140 s)$$

$$\frac{1}{[A]^2} = 29.56 M^{-2}$$

$$[A]^2 = 0.0338 M^2$$

$[A] = 0.184 M \approx$ **0.18 M**