General Chemistry II
July 30, 2020

Exam 2 Review

1. **The pH of a 0.063 M solution of hypobromous acid (HOBr) is 4.95. Calculate K_a.**

$$HOBr(aq) + H_2O(l) \leftrightarrow OBr^-(aq) + H_3O^+(aq)$$

	HOBr	OBr^-	H_3O^+
I	0.063	0	0
C	-x	+x	+x
E	0.063-x	x	x

Since the pH is given, the equilibrium H_3O^+ concentration can be calculated.

$$pH = -\log[H_3O^+]_{eq}$$

$$[H_3O^+]_{eq} = 10^{-pH} = 10^{-4.95} = 1.122 * 10^{-5}\ M$$

Based on the ICE table above, the equilibrium hydronium concentration is represented by x, so x = 1.122×10^{-5} M.

$$K_a = \frac{[H_3O^+][OBr^-]}{[HOBr]} = \frac{(1.122 * 10^{-5}\ M)(1.122 * 10^{-5}\ M)}{(0.063\ M - 1.122 * 10^{-5}\ M)} = 2 * 10^{-9}$$

2. **Arrange the following 0.10 M solutions in order from most acidic to most basic.**
KOH, KCl, KCN, NH_4Cl, HCl

First recognize that there is a strong acid (HCl) and strong base (KOH) in this group. This will be the most acidic and basic solutions, respectively.

KCl is a neutral salt, because Cl^- is a weak conjugate base of a strong acid, and K^+ doesn't have an affinity to accept protons, and it cannot produce protons.

Regarding KCN, K^+ has just been established to have no effect on pH. CN^- is the conjugate base of a weak acid, so it can react with water.

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

Since OH^- is being produced, this would be a basic solution.

Finally, regarding NH_4Cl, Cl^- has no effect on pH. NH_4^+ is the conjugate acid of a weak base and can thus react with water.

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$

Since H_3O^+ is produced, this solution is slightly acidic.

Thus, the final ordering is: HCl, NH_4Cl, KCl, KCN, KOH

3. **An unknown salt is either NaCN, $NaC_2H_3O_2$, NaF, NaCl, or NaOCl. When 0.100 mol of the salt is dissolved in 1.00 L of water, the pH of the solution is 8.07. What is the identity of the salt?**

Since Na^+ does not accept protons and cannot produce protons, it does not affect pH. Generally, we have:

$$A^-(aq) + H_2O(l) \leftrightarrow HA(aq) + OH^-(aq)$$

	A^-	HA	OH^-
I	0.100	0	0
C	-x	+x	+x
E	0.100 - x	x	x

Based on the pH of the solution, the equilibrium OH^- concentration can be determined.

$$pOH = 14 - pH = 14 - 8.07 = 5.93$$

$$[OH^-]_{eq} = x = 10^{-5.93} = 1.17 * 10^{-6}$$

$$K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{(1.17 * 10^{-6}\ M)(1.17 * 10^{-6}\ M)}{(0.100M - 1.17 * 10^{-6}\ M)} = 1.38 * 10^{-11}$$

This is very close to the K_b in the table for F^-, so the identity of the salt is NaF

4. **100.0 mL of 0.10 M malonic acid (HOOC-CH2-COOH) is titrated with 0.10 M NaOH. K_{a1} = 1.5 x 10^{-3} and K_{a2} = 2.0 x 10^{-6}.**
   a. **Write out the reactions and equilibrium expressions associated with K_{a1} and K_{a2}**

      Note that these reactions are not the ones reflecting the titration!! They are reflective of the ionization constants.

      K_{a1}:

$$HOOC - CH_2 - COOH(aq) + H_2O(l) \leftrightarrow HOOC - CH_2 - COO^-(aq) + H_3O^+(aq)$$

$$K_{a1} = \frac{[H_3O^+][HOOC - CH_2 - COO^-]}{[HOOC - CH_2 - COOH]} = 1.5 * 10^{-3}$$

      K_{a2}:

$$HOOC - CH_2 - COO^-(aq) + H_2O(l) \leftrightarrow O^-OC - CH_2 - COO^-(aq) + H_3O^+(aq)$$

$$K_{a1} = \frac{[H_3O^+][O^-OC - CH_2 - COO^-]}{[HOOC - CH_2 - COO^-]} = 2.0 * 10^{-6}$$

   b. **Calculate the pH:**
      i. **Before any NaOH is added**

         Before starting any calculations, it's useful to determine at what volumes the half-equivalence and equivalence points will occur at. Since the molarities are the same, and the base and OH^- are in a 1:1 ratio, along with the acid to the base, 100.0 mL of NaOH is required to completely neutralize one proton on the malonic acid. Another 100 mL of NaOH must be added to neutralize the second proton. Thus, the first equivalence point occurs after adding 100 mL of NaOH, the second after adding 200 mL. The first half equivalence point occurs at 50 mL, the second at 150 mL.

$$HOOC-CH_2-COOH(aq)+H_2O(l) \leftrightarrow HOOC-CH_2-COO^-(aq)+H_3O^+(aq)$$

	$HOOC-CH_2-COOH$	$HOOC-CH_2-COO^-$	H_3O^+
I	0.100	0	0
C	-x	+x	+x
E	0.100 - x	x	x

$$K_{a1}=\frac{[H_3O^+][HOOC-CH_2-COO^-]}{[HOOC-CH_2-COOH]}=1.5*10^{-3}=\frac{x^2}{0.100-x}$$

$$x^2=1.5*10^{-4}-1.5*10^{-3}x$$

$$x^2+1.5*10^{-3}x-1.5*10^{-4}=0$$

After using quadratic formula, x = -0.0130204 and x = 0.0115204

$$x=[H_3O^+]_{eq}=0.0115204\ M$$

$$pH=-\log[H_3O^+]=-\log(0.0115204\ M)=1.94$$

ii. **After 50 mL of NaOH is added**

This is the first half equivalence point, so

$$pH=pK_{a1}=-\log(K_{a1})=-\log(1.5*10^{-3})=2.82$$

iii. **After 100 mL of NaOH is added**

This is the first equivalence point, so

$$pH=\frac{pK_{a1}+pK_{a2}}{2}=\frac{2.82-\log(K_{a2})}{2}=\frac{2.82+5.70}{2}=4.26$$

iv. **After 150 mL of NaOH is added**

This is the second half equivalence point, so

$$pH = pK_{a2} = -\log(K_{a2}) = -\log(2.0 * 10^{-6}) = 5.70$$

v. **After 200 mL of NaOH is added**

This is the second equivalence point. Thus, the main reaction of interest is:

$$O^-OC - CH_2 - COO^-(aq) + H_2O(l) \leftrightarrow HOOC - CH_2 - COO^-(aq) + OH^-(aq)$$

The initial molarity of $O^-OC\text{-}CH_2\text{-}COO^-$ is found by dividing the number of moles (0.01) 0.3 L of total solution.

	$O^-OC\text{-}CH_2\text{-}COO^-$	$HOOC\text{-}CH_2\text{-}COO^-$	OH^-
I	0.0333	0	0
C	-x	+x	+x
E	0.033 - x	x	x

$$K_b = \frac{1 * 10^{-14}}{K_{a2}} = \frac{1 * 10^{-14}}{2 * 10^{-6}} = 5 * 10^{-9}$$

$$K_b = 5 * 10^{-9} = \frac{[OH^-][HOOC - CH_2 - COO^-]}{[O^-OC - CH_2 - COO^-]} = \frac{x^2}{0.033 - x}$$

$$x^2 = 1.65 * 10^{-10} - 5 * 10^{-9}x$$

$$x^2 + 5 * 10^{-9}x - 1.65 * 10^{-10} = 0$$

From the quadratic formula, we get the answer:

$$x = 1.28 * 10^{-5}$$

$$pOH = -\log[OH^-] = -\log(1.28 * 10^{-5}\ M) = 4.89$$

$$pH = 14 - pOH = 14 - 4.89 = 9.11$$

5. **You are asked to prepare a pH = 3.00 buffer solution starting from 1.25 L of a 1.00 M solution of HF and any amount you need of NaF**
   a. **What is the pH of the HF solution prior to adding NaF?**

$$HF(aq) + H_2O(aq) \leftrightarrow F^-(aq) + H_3O^+(aq)$$

	HF	F^-	H_3O^+
I	1	0	0
C	-x	+x	+x
E	1 - x	x	x

$$K_a = 7.2 * 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{1-x}$$

$$x^2 = 7.2 * 10^{-4} - 7.2 * 10^{-4}x$$

$$x^2 + 7.2 * 10^{-4}x - 7.2 * 10^{-4} = 0$$

From the quadratic equation, x = 0.0264752 M.

$$pH = -\log[H_3O^+]_{eq} = -\log(x) = -\log(0.0264752) = 1.58$$

   b. **How many grams of NaF should be added to prepare the buffer solution? Neglect the small volume change that occurs when the NaF is added.**

$$pH = pK_a + \log\left(\frac{[F^-]}{[HF]}\right)$$

$$3.00 = -\log(7.2 * 10^{-4}) + \log\left(\frac{[F^-]}{[HF]}\right)$$

$$\frac{[F^-]}{[HF]} = 0.72$$

Since the change in volume after adding NaF is negligible, that does not have to be taken into account.

$$\frac{[F^-]}{1.00\ M} = 0.72$$

$$[F^-] = 0.72\ M$$

$$\frac{0.72\ mol\ F^-}{L} * 1.25\ L * \frac{1\ mol\ NaF}{1\ mol\ F^-} * \frac{41.99\ g\ NaF}{1\ mol\ NaF} = 37.79\ g\ NaF$$

6. You titrate 25.0 mL of 0.10 M NH_3 with 0.10 M HCl. (NH_3 $K_b = 1.8 \times 10^{-5}$)

(a) What is the pH of the NH_3 solution before the titration begins?

	$NH_3(aq)$	$+\ H_2O(l)$	$\rightleftharpoons NH_4^+(aq)$	$+\ OH^-(aq)$
I	0.10		0	0
C	$-x$		$+x$	$+x$
E	$0.10-x$		x	x

$1.8 \times 10^{-5} = \dfrac{x^2}{.10-\cancel{x}}$

$x = 1.3 \times 10^{-3}$

$[OH^-] = x$

$pOH = -\log(1.3 \times 10^{-3}) = 2.87$ $pH = 14 - pOH = 14 - 2.87 = \boxed{11.13}$

(b) What is the pH at the equivalence point?

moles NH_3 = .10 M × .025 L = .0025 moles

At equivalence point: moles NH_3 = moles HCl

V_{HCl} needed = .0025 mol / 0.10 M = .025 L

Total V = .025 L + .025 L = .050 L

$[NH_4^+]_i = \dfrac{.0025\text{ mol}}{.050\text{ L}} = .05\text{ M}$

NH_4^+ $K_a = 1 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

	$NH_4^+(aq)$	$+\ H_2O(l)$	$\rightleftharpoons NH_3(aq)$	$+\ H_3O^+(aq)$
I	.05		0	0
C	$-x$		$+x$	$+x$
E	$.05-x$		x	x

$K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]}$

$5.6 \times 10^{-10} = \dfrac{x^2}{.05-\cancel{x}}$

$x = 5.3 \times 10^{-6}$

$[H_3O^+] = x$

$pH = -\log[5.3 \times 10^{-6}]$

$= \boxed{5.28}$

(c) What is the pH at the half equivalence point of the titration?

At half equivalence point

$pOH = pK_b = -\log(1.8 \times 10^{-5}) = 4.74$

$pH = 14 - pOH = 14 - 4.74 = \boxed{9.26}$

(d) Calculate the pH of the solution after adding 5.00, 15.0, 20.0, 22.0, and 30.0 mL of the acid.

25.0 mL is equivalence point. For 5.00, 15.0, 20.0, and 22.0 it is in the buffer region (Use Henderson Hasselbach). For the 30.0 mL, there is excess HCl

For HH, can use moles instead of [ ] because V cancels in ration since it is the same.

	mL .10 M HCl	5.00	15.0	20.0	22.0
n_a	moles HCl	.0005	.0015	.0020	.0022
n_b	moles NH_3	.0020	.0010	0.005	.0003
	pH	9.86	9.08	8.66	8.39

moles HCl = n_a = .10 M × V

n_b = .0025 − n_a

$pH = pK_a + \log \dfrac{n_b}{n_a}$

$= 9.26 + \log \dfrac{n_b}{n_a}$

30.0 mL of acid means 5.0 mL excess of HCl

Total V = 55.0 mL

moles excess HCl = .005 L × .10 M = .0005 moles

$[HCl] = \dfrac{.0005\text{ mol}}{.055\text{ L}} = .0091\text{ M} = [H_3O^+]$

$pH = -\log(.0091) = \boxed{2.04}$