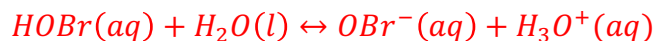


Exam 2 Review

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



	HOBr	OBr ⁻	H ₃ O ⁺
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.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]_{eq}$$

$$[\text{H}_3\text{O}^+]_{eq} = 10^{-\text{pH}} = 10^{-4.95} = 1.122 \times 10^{-5} \text{ M}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OBr}^-]}{[\text{HOBr}]} = \frac{(1.122 \times 10^{-5} \text{ M})(1.122 \times 10^{-5} \text{ M})}{(0.063 \text{ M} - 1.122 \times 10^{-5} \text{ M})} = 2 \times 10^{-9}$$

2. Arrange the following 0.10 M solutions in order from most acidic to most basic.
KOH, KCl, KCN, NH₄Cl, 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.



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.

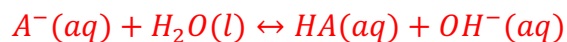


Since H_3O^+ is produced, this solution is slightly acidic.

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^-	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.

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

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

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

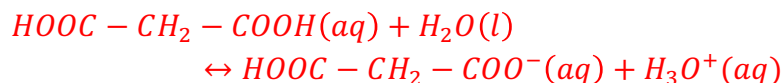
This is very close to the K_b in the table for F^- , so the identity of the salt is NaF

4. 100.0 mL of 0.10 M malonic acid ($\text{HOOC}-\text{CH}_2-\text{COOH}$) is titrated with 0.10 M NaOH. $K_{a1} = 1.5 \times 10^{-3}$ and $K_{a2} = 2.0 \times 10^{-6}$.

a. Write out the reactions and equilibrium expressions associated with K_{a1} and K_{a2}

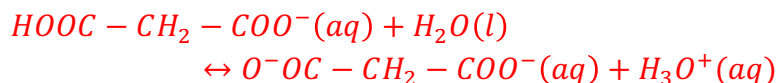
Note that these reactions are not the ones reflecting the titration!! They are reflective of the ionization constants.

K_{a1} :



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HOOC}-\text{CH}_2-\text{COO}^-]}{[\text{HOOC}-\text{CH}_2-\text{COOH}]} = 1.5 \times 10^{-3}$$

K_{a2} :

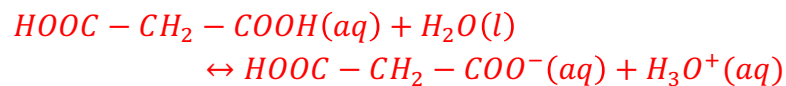


$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{O}^-\text{OC}-\text{CH}_2-\text{COO}^-]}{[\text{HOOC}-\text{CH}_2-\text{COO}^-]} = 2.0 \times 10^{-6}$$

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	HOOC-CH ₂ -COO ⁻	H ₃ O ⁺
I	0.100	0	0
C	-x	+x	+x
E	0.100 - x	x	x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HOOC} - \text{CH}_2 - \text{COO}^-]}{[\text{HOOC} - \text{CH}_2 - \text{COOH}]} = 1.5 * 10^{-3} = \frac{x^2}{0.100 - x}$$

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

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

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

$$x = [\text{H}_3\text{O}^+]_{eq} = 0.0115204 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0115204 \text{ M}) = 1.94$$

ii. After 50 mL of NaOH is added

This is the first half equivalence point, so

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

iii. After 100 mL of NaOH is added

This is the first equivalence point, so

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

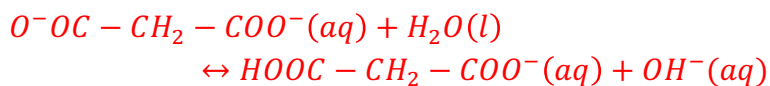
iv. After 150 mL of NaOH is added

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:



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

	$O^-OC-CH_2-COO^-$	$HOOC-CH_2-COO^-$	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	F ⁻	H ₃ O ⁺
I	1	0	0
C	-x	+x	+x
E	1 - x	x	x

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

$$x^2 = 7.2 \times 10^{-4} - 7.2 \times 10^{-4}x$$

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

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.

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

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

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

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

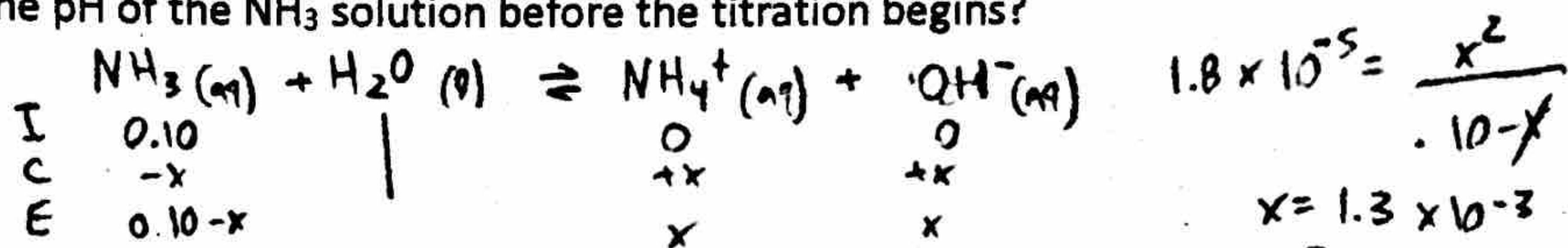
$$\frac{[F^-]}{1.00\text{ }M} = 0.72$$

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

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

6. You titrate 25.0 mL of 0.10 M NH_3 with 0.10 M HCl . ($\text{NH}_3 K_b = 1.8 \times 10^{-5}$)

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



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

$$[\text{OH}^-] = x$$

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

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

$$\text{moles NH}_3 = 0.10 \text{ M} \times 0.025 \text{ L} = 0.0025 \text{ moles}$$

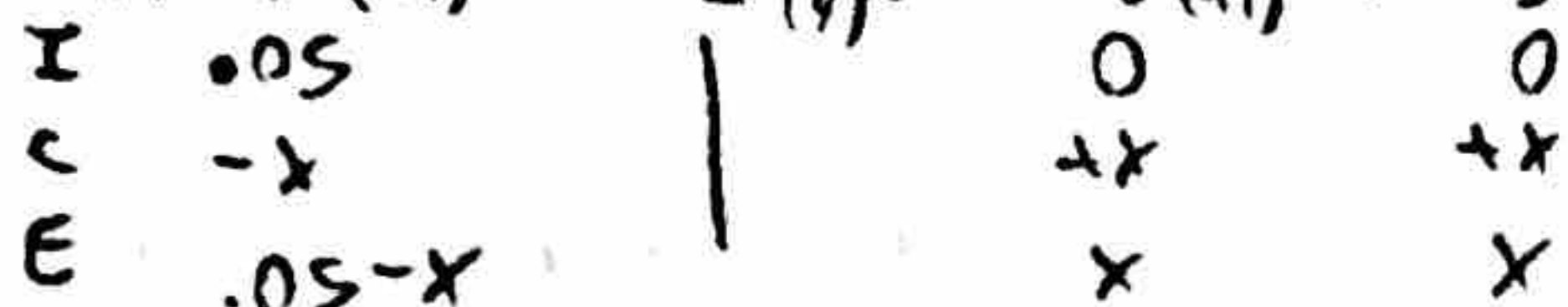
At equivalence point: moles NH_3 = moles HCl

$$[\text{NH}_4^+]_i = \frac{0.0025 \text{ mol}}{0.050 \text{ L}} = 0.05 \text{ M}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$V_{\text{HCl needed}} = 0.0025 \text{ mol} / 0.10 \text{ M} = 0.025 \text{ L}$$

$$\text{Total V} = 0.025 \text{ L} + 0.025 \text{ L} = 0.050 \text{ L}$$



$$5.6 \times 10^{-10} = \frac{x^2}{0.05-x}$$

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

$$[\text{H}_3\text{O}^+] = x$$

$$\text{pH} = -\log(5.3 \times 10^{-6})$$

$$= \boxed{5.28}$$

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

At half equivalence point

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

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

(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 ratio since it is the same.

mL 0.10 M HCl	5.00	15.0	20.0	22.0
n_a moles HCl	0.0005	0.0015	0.0020	0.0022
n_b moles NH_3	0.0020	0.0010	0.0005	0.0003
pH	9.86	9.08	8.66	8.39

$$\text{moles HCl} = n_a = 0.10 \text{ M} \times V$$

$$n_b = 0.0025 - n_a$$

$$\text{pH} = \text{p}K_a + \log \frac{n_b}{n_a}$$

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

Total $V = 55.0 \text{ mL}$

30.0 mL of acid means 5.0 mL excess of HCl

$$\text{moles excess HCl} = 0.005 \text{ L} \times 0.10 \text{ M} = 0.0005 \text{ moles}$$

$$[\text{HCl}] = \frac{0.0005 \text{ mol}}{0.055 \text{ L}} = 0.0091 \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0091) = \boxed{2.04}$$