WORKSHEET: SOLUTION EQUILIBRIUM (Weak acids and bases, buffers, Polyprotic acids, and Hydrolysis.)

SET A:

mol HCl = mol CH_3NH_2

1. 40.00 ml of 0.350 M CH_3NH_2 is titrated with 0.280 M HCl until the end point is reached . Calculate the pH of the solution at the end point.(K_b for CH_3NH_2= 5.0×10^{-4})

Setup:

1st Calc Vol_{HCl} added to equivalence pt

$$.04000\,L \times \frac{.350\ mol\ CH_3NH_2}{L} \times \frac{1\ mol\ HCl}{1\ mol\ CH_3NH_2} \times \frac{1\ L}{.280\ mol\ HCl}$$

$$= .0500\,L\ HCl$$ added to equivalence pt.

2nd Acid-Base Neutralization rxn

	WB CH_3NH_2	+	SA (LR) HCl	→	$CH_3NH_3^+$	+ H_2O
B	$.0400\,L \times .350\ mol/L$ = .0140 mol		$.0500\,L \times .280\ mol/L$ = .0140 mol		Ø	
Δ	−.0140		−.0140		+.0140	
After	Ø		Ø		.0140 mol $CH_3NH_3^+$ CA	

3rd Equilibrium

	$CH_3NH_3^+$	+ H_2O ⇌	CH_3NH_2	+ H_3O^+
I	$\frac{.0140}{(.0400+.0500)}$		Ø	Ø
C	−x		+x	+x
E	(.156 − x)		(x)	(x)

$$K_a = \frac{K_w}{K_b\ CH_3NH_2} = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]}$$

$$K_a = \frac{10^{-14}}{5.0 \times 10^{-4}} = \frac{(x)(x)}{.156 - x \rightarrow \text{neg}}$$

Answer: 5.74

$$[H_3O^+] = x = 1.8 \times 10^{-6}$$

$$pH = -\log 1.8 \times 10^{-6} = 5.74$$

Approx

$.156 - x \approx .156$

∴ x is neg

$\frac{1.8 \times 10^{-6}}{.156}(100) < 5\%$

∴ x is neg!

BA

CB NO_2^-

2. How many moles of HNO_2 must be added to a 1.00 liter of 0.370 M $NaNO_2$ to give a buffer of pH= 4.20? (Ignore any volume change due to the addition of HNO_2) (K_a for HNO_2 is 4.5×10^{-4}).

Setup:

	HNO_2	+ H_2O	⇌	H_3O^+	+ NO_2^-
I	S			∅	.370
C	$-10^{-4.20}$			$+10^{-4.20}$	$+10^{-4.20}$
E	$S-10^{-4.20}$			$(10^{-4.20})$	$(.370-10^{-4.20})$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$4.5\times10^{-4} = \frac{(10^{-4.20})(.370+10^{-4.20})}{S-10^{-4.20}}$$

$S = 0.052$ mol/L HNO_2

Approx

$S - 10^{-4.20} \approx S$

$\frac{10^{-4.20}}{.052}(100) < 5\%$

Answer: 0.052 moles

3. a. Is $NaHCO_3$ (aq) acidic, basic, or neutral ?You must show your work to justify your answer. (K_{a1} for H_2CO_3 = 4.3 x 10-7, Ka_2 for HCO_3^- = 4.8×10^{-11})

Setup:

① eqns → BA → CB ② Calc K_b for CB ③ Ka vs K_b ④ A or B

BA $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ $Ka_2 = 4.8\times10^{-11}$

CB $HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$ $K_b = \frac{K_w}{Ka_1 H_2CO_3}$

$= \frac{10^{-14}}{4.3\times10^{-7}}$

$= 2.3 \times 10^{-8}$

$Kb > Ka_2$ ∴ Basic

Answer: K_b for HCO_3^- is larger than Ka_2 for HCO_3^-, $NaHCO_3$ (aq) is basic.

b

Setup:

SA $H^+ + HCO_3^- \longrightarrow H_2CO_3$

SB $OH^- + HCO_3^- \longrightarrow H_2O + CO_3^{2-}$

HCO_3^- can "behave / act" as a buffer

SB

LR!

4. How many moles of NaOH must be added to a 1.00 liter of 0.230 M benzoic acid, $HC_7H_5O_2$, to produce a solution of pH = 4.50? (Ka for $HC_7H_5O_2$ = 6.3 x 10^{-5})

Setup:

Rxn 1st

	$NaOH$	+	$HC_7H_5O_2$	→	$C_7H_5O_2^-$	+	H_2O
Before	u		1 L x .230 mol/L = .230 mol		$\emptyset$		
Δ	$-u$		$-u$		$+u$		
After	$\emptyset$		$.230-u$ $HC_7H_5O_2$ BA		u $C_7H_5O_2^-$ CB		

Equilib 2nd

	$HC_7H_5O_2$	+	H_2O	⇌	$C_7H_5O_2^-$	+	H_3O^+
I	$.230-u$				u		$\emptyset$
C	$-10^{-4.50}$				$+10^{-4.50}$		$+10^{-4.50}$
E	$.230-u-10^{-4.50}$				$u+10^{-4.50}$		$10^{-4.50}$

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]}$$

$$6.3\times10^{-5} = \frac{(3.2\times10^{-5})(u+10^{-4.50})}{.230-u-10^{-4.50}}$$

neg

neg

Answer: ~~0.15 mole~~ → $u = .15$ mol $C_7H_5O_2^-$

5) The $[S^{2-}]$ concentration of a 0.150 M H_2S is adjusted to a value of 4.18×10^{-8} moles/liter. What is the $[H^+]$ concentration?

(K_{a1} for H_2S = 8.9×10^{-8}, K_{a2} for HS^- is 1.2×10^{-13})

Setup:

Equilib

H_2S S^{2-}

$$H_2S + 2H_2O \rightleftharpoons S^{2-} + 2H_3O^+$$

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+ \quad K_{a_1}$$

$$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+ \quad K_{a_2}$$

$$H_2S + 2H_2O \rightleftharpoons S^{2-} + 2H_3O^+ \quad K_{overall} = K_{a_1} \times K_{a_2}$$

	H_2S	+	$2H_2O$	⇌	S^{2-}	+	$2H_3O^+$
E	.150				4.18×10^{-8}		? H_3O^+ ?

Answer: 1.9×10^{-7} M

$$K_{overall} = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]}$$

$$K_{a_1} \times K_{a_2} = (8.9\times10^{-8})(1.2\times10^{-13}) = \frac{[H_3O^+]^2(4.18\times10^{-8})}{.150}$$

$$[H_3O^+] = 1.9\times10^{-7}\ M$$

6. What is the $[H^+]$ concentration of a solution made by adding 35.00 ml of 0.660 M $C_6H_5NH_2$ (WB) to 40.00 ml of 0.420 M HCl? (SA) (K_b for $C_6H_5NH_2$ is 4.6×10^{-7})

Setup:

1st Rxn -> moles

	HCl	+	$C_6H_5NH_2$	→	$C_6H_5NH_3^+$
B:	$.0400\,L \times .420\,\frac{mol}{L} = .0168\,mol$		$.03500\,L \times .660\,\frac{mol}{L} = .0231\,mol$		∅
Δ	$-.0168$		$-.0168$		$+.0168$
A	∅ HCl = LR!		$.0063\,mol$ $C_6H_5NH_2$ WB		$.0168\,mol$ $C_6H_5NH_3^+$ CA

export to equilibria

2nd Equilibria -> M

	$C_6H_5NH_2$	+ H_2O ⇌	$C_6H_5NH_3^+$	+ OH^-
I	$\frac{.0063\,mol}{(.0400+.03500)L}$		$\frac{.0168\,mol}{(.0400+.03500)L}$	∅
C	$-x$		$+x$	$+x$
E	$(.0840-x)$		$(.224+x)$	$+x$

K_b calc

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

$$4.6 \times 10^{-7} = \frac{(.224 + \cancel{x})(x)}{(.0840 - \cancel{x})}$$ (x neg; x neg)

$$[OH^-] = x = 1.7 \times 10^{-7}\,M$$

$$[H^+] = 5.9 \times 10^{-8}\,M$$

Approx

$.224 + x \approx .224$

$.0840 - x \simeq .0840$

Answer: 5.9×10^{-8} M

$\frac{1.7 \times 10^{-7}}{.224}(100) < 5\%$

$\frac{1.7 \times 10^{-7}}{.0840}(100) < 5\%$

x is neg!

7. Predict whether the following solutions are acidic, basic, or neutral. Write the equilibrium equations, and all calculations if needed, to justify your answer. (K_b for NH_3 is 1.8×10^{-5}, K_a for HClO is 3.5×10^{-8})

1) eqno 2) calc Ka & Kb 3) compare Ka to Kb 4) (A) or (B)

a. NH_4ClO

Setup:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (CA)

$K_a = \frac{K_w}{K_b\ NH_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 6 \times 10^{-10}$

$ClO^- + H_2O \rightleftharpoons HClO + OH^-$ (CB)

$K_b = \frac{K_w}{K_a\ HClO} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}$

Answer: K_b for ClO^- > Ka for NH_4^+ , Basic

b. $NaNO_2$

Setup:

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ (CB)

Answer: Basic

c. $Ni(NO_3)_3$

Setup:

$Ni^{3+} + H_2O \rightleftharpoons NiOH^{2+} + H^+$

or $Ni(H_2O)_6^{3+} + H_2O \rightleftharpoons Ni(H_2O)_5OH^{2+} + H_3O^+$

Answer: Acidic

SET B:

1. How many moles of $HCHO_2$ (WA) must be added to a 1.00 liter of 0.400 M $NaCHO_2$ (CHO_2^-, CB) to give a buffer of pH= 3.60? Ignore any volume change due to the addition of $HCHO_2$. (Ka for $HCHO_2$=1.8×10^{-4})

Setup:

	$HCHO_2$	+ H_2O ⇌	CHO_2^-	+ H_3O^+
I	w		.400	∅
C	$-10^{-3.60}$		$+10^{-3.60}$	$+10^{-3.60}$
E	$w - 10^{-3.60}$		$(.400 + 10^{-3.60})$	$(10^{-3.60})$

$K_a = \frac{[CHO_2^-][H_3O^+]}{[HCHO_2]}$

$1.8 \times 10^{-4} = \frac{(.400 + 10^{-3.60})(10^{-3.60})}{(w - 10^{-3.60})}$ → neg

Approx

$w - 10^{-3.60} \approx w$

$\frac{10^{-3.60}}{.55}(100) < 5\%$

$\therefore 10^{-3.60}$ is neg !

$M_{HCHO_2} = w = .55\ M$

Answer: 0.55 mole

$1.00\ L \times \frac{.55\ mol\ HCHO_2}{L} = .55\ mol\ HCHO_2$

2. (a.)

Setup:

$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$ (CB)

$HPO_4^{2-} + OH^- \rightarrow H_2O + PO_4^{3-}$ (WA)

HPO_4^{2-}

Answer: Yes

(b.) Is ~~Na_2HPO_4~~ acidic, basic, or neutral? You must show your work to justify your answer.

K_{a3} for HPO_4^{2-} is 1.00×10^{-12}, K_{a2} for $H_2PO_4^-$ is 6.2×10^{-8}

Setup:

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$ $\quad K_{a_3} = 1.00 \times 10^{-12}$

$HPO_4^{2-} + H_2O \rightleftharpoons OH^- + H_2PO_4^-$ $\quad K_b = \frac{K_w}{K_a \text{ of } H_2PO_4^-} = \frac{10^{-14}}{6.2 \times 10^{-8}}$

$K_b = 2.9 \times 10^{-7}$

$K_b > K_{a_3}$ ∴ basic

Answer: K_b (for HPO_4^{2-}) > K_{a3} (for HPO_4^{2-}), Basic

3. What is the $[H^+]$ concentration of a solution made by titrating 30.00 ml of 0.7200 M $C_6H_5NH_2$ with 0.2500 M HCl until the equivalence point is reached? K_b for $C_6H_5NH_2$ is 4.6×10^{-7}.

Setup: SA

"end point"

mol A = mol B

1st Rxn → moles

$HCl + C_6H_5NH_2 \rightarrow C_6H_5NH_3^+$

B: $\square$ L $\times .2500 \frac{mol}{L}$ $\quad .0300 L \times .7200 \frac{mol}{L}$ $\quad \not\emptyset$

$= .0216$ mol $\quad = .0216$ mol (same)

Δ $\quad -.0216 \quad -.0216 \quad +.0216$

After: $\not\emptyset$ HCl = LR! $\quad \not\emptyset$ $C_6H_5NH_2$ $\quad .0216$ mol $C_6H_5NH_3^+$

2nd Equilibrium → M (export to equilibria)

(CA)

	$C_6H_5NH_3^+$	+ H_2O ⇌	H_3O^+	+ $C_6H_5NH_2$
I	$\frac{.0216 \text{ mol}}{(.0864 + .0300) L}$		$\not\emptyset$	$\not\emptyset$
C	$-x$		$+x$	$+x$
E	$(.1856 - x)$		(x)	(x)

$K_a = \frac{K_w}{K_b \, C_6H_5NH_2} = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$ Answer: 6.4×10^{-5}

-6-

$\frac{10^{-14}}{4.6 \times 10^{-7}} = \frac{(x)(x)}{(.1856 - x)}$ neg

$[H_3O^+] = x = 6.4 \times 10^{-5}$ M

Approx: $.1856 - x \approx .1856$

$\frac{6.4 \times 10^{-5}}{.1856}(100) < 5\%$

∴ x is neg!

4. Predict whether each of the following solutions is acidic, basic, or neutral. Write the equilibrium equations, and all calculations if needed, to justify your answer. K_b for NH_3= 1.8×10^{-5}, K_a for $HCHO_2$ is 1.8×10^{-4}.

a. NH_4CHO_2
Setup:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $\quad K_a = \frac{K_w}{K_b\,NH_3} = \frac{10^{-14}}{1.8\times10^{-5}}$

$K_a = 5.5\times10^{-10}$

$K_a > K_b$ ∴ Acidic

$CHO_2^- + H_2O \rightleftharpoons HCHO_2 + OH^-$ $\quad K_b = \frac{K_w}{K_a\,HCHO_2} = \frac{10^{-14}}{1.8\times10^{-4}}$

$K_b = 5.5\times10^{-11}$

Answer: K_a (for NH_4^+) > Kb (for CHO_2^-) , Acidic

b. ~~Na_2S~~
Setup:

$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$

CB

↑ Basic!

Answer: Basic

c. $Cr(NO_3)_3$
Setup:

$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^+$

or $Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{2+} + H_3O^+$

Answer: Acidic

5. The $C_6H_6O_6^{2-}$, ascorbate ion, concentration of a 0.270 M ascorbic acid, is adjusted to a value of 8.5×10^{-8} mole/liter. What is the $[H^+]$ concentration? K_{a1} for $H_2C_6H_6O_6$ is 7.9×10^{-5} and K_{a2} for $HC_6H_6O_6^-$ is 1.6×10^{-12}.
Setup:

$C_6H_6O_6^{2-} \xleftrightarrow{\text{Look!}} H_2C_6H_6O_6$

K_{a_1}

$H_2C_6H_6O_6 + H_2O \rightleftharpoons HC_6H_6O_6^{-1} + H_3O^+$ $\quad K_{a_1}$

$HC_6H_6O_6^{-1} + H_2O \rightleftharpoons C_6H_6O_6^{2-} + H_3O^+$ $\quad K_{a_2}$

$H_2C_6H_6O_6 + 2H_2O \rightleftharpoons C_6H_6O_6^{2-} + 2H_3O^+$ $\quad K_{a_1}\times K_{a_2}$

.270 $\qquad 8.5\times10^{-8} \qquad ?$

$K_{overall} = K_{a_1} \times K_{a_2} = \frac{[C_6H_6O_6^{2-}]\,[H_3O^+]^2}{[H_2C_6H_6O_6]}$

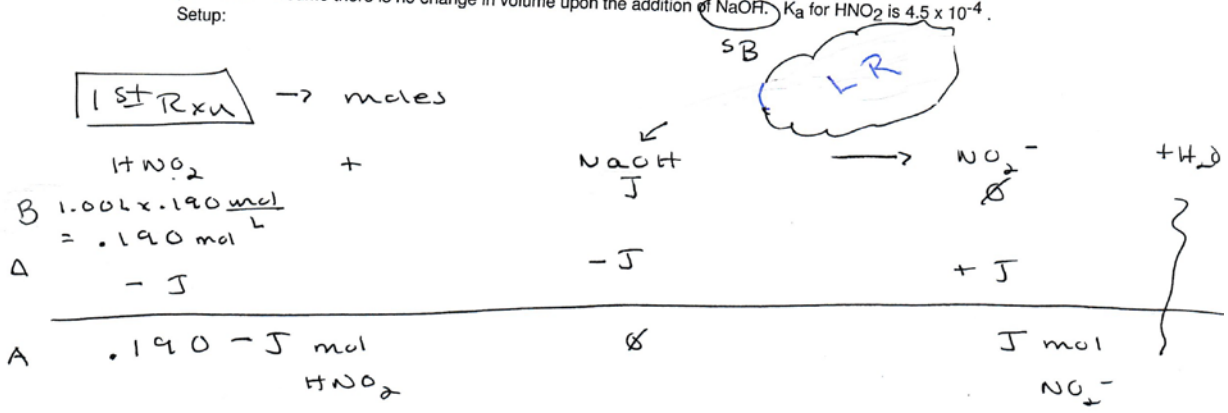
$(7.9\times10^{-5})(1.6\times10^{-12}) = \frac{(8.5\times10^{-8})\,[H_3O^+]^2}{(.270)}$

$[H_3O^+] = 2.0\times10^{-5}$

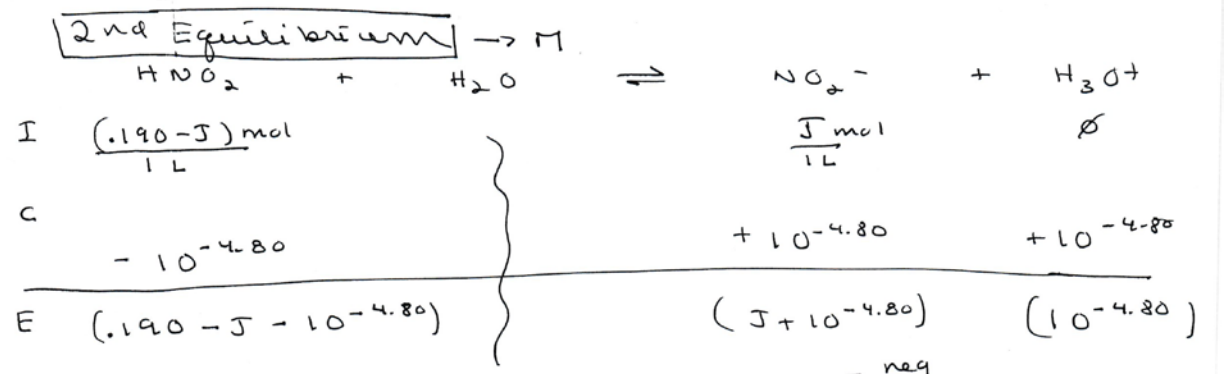
Answer: 2.0×10^{-5} M

6. How many moles of NaOH should be added to a 1.00 liter of 0.190 M HNO_2 to produce a solution of pH= 4.80? Assume there is no change in volume upon the addition of NaOH. K_a for HNO_2 is 4.5×10^{-4}.

Setup:



Export



$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(J + 10^{-4.80})(10^{-4.80})}{(.190 - J - 10^{-4.80})}$$

(J + 10^-4.80): neg

(.190 − J − 10^-4.80): neg

$J = .18$ M NaOH

$J = .18$ mol NaOH

Approx.

$J + 10^{-4.80} \approx J$

$.190 - J - 10^{-4.80} \approx .190$

Answer: 0.18 mole

$\frac{1.58 \times 10^{-5}}{.18}(100) < 5\%$

$\frac{1.58 \times 10^{-5}}{.190 - .18}(100) < 5\%$

7) What is the pH of a solution made by mixing 25.00 ml of 0.440 M CH_3NH_3Cl and 37.00 ml of .200 M NaOH? 0.200 M NaOH? K_b for CH_3NH_2 is 5.0×10^{-4}.

LR ↓ (NaOH)

SB ↑ (NaOH)

Setup:

1st Rxn → mol

LR ↓

	$CH_3NH_3^+$	+	NaOH	→	CH_3NH_2
B	$.02500\,L \times .440 \frac{mol}{L}$ = 0.0110 mol		$.03700\,L \times .200 \frac{mol}{L}$ = 7.40×10^{-3} mol		∅
Δ	-7.40×10^{-3}		-7.40×10^{-3}		$+7.40 \times 10^{-3}$
A	3.60×10^{-3} mol $CH_3NH_3^+$		∅		7.40×10^{-3} CH_3NH_2

2nd Equilibrium → M

Use Henderson - Hasselbach!

$$pH = pKa + \log \frac{[A^-]}{[HA]}$$

$$pH = -\log \frac{K_w}{K_b} + \log \frac{[CH_3NH_3^+]}{[CH_3NH_2]}$$

$$pH = \log \left(\frac{10^{-14}}{5.0 \times 10^{-4}} \right) + \log \frac{7.40 \times 10^{-3}\ mol / .062\ L}{3.60 \times 10^{-3}\ mol / .062\ L}$$

$$= 11.00$$

Answer: pH= 11.00

SET C:

1. The oxalate ion concentration, $C_2O_4^{2-}$ of 0.20 M $H_2C_2O_4$ is adjusted to a value of 3.00×10^{-3} M. What is the $[H^+]$ ion concentration in the solution? K_{a1} for $H_2C_2O_4$ is 5.6×10^{-2} and K_{a2} for $HC_2O_4^-$ is 5.1×10^{-5}.

Setup:

K_{a_1} $H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$

K_{a_2} $HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$

$H_2C_2O_4 + 2H_2O \rightleftharpoons 2H_3O^+ + C_2O_4^{2-}$

$K_3 = K_{a_1} \times K_{a_2}$

$$K_3 = \frac{[H_3O^+]^2[C_2O_4^{2-}]}{[H_2C_2O_4]}$$

$$(5.6 \times 10^{-2})(5.1 \times 10^{-5}) = \frac{[H_3O^+]^2 (3.00 \times 10^{-3})}{(.20)}$$

$$[H_3O^+] = 1.4 \times 10^{-2} M$$

Answer: 1.4×10^{-2} M

2. Predict whether each of the following solutions is acidic, basic, or neutral. Write the equilibrium equations, and all calculations if needed, to justify your answer. Kb for NH_3 is 1.8×10^{-5}, K_a for HClO is 3.5×10^{-8}.

a. NH_4ClO

Setup:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (CA)

$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}}$

$K_a = 5.5 \times 10^{-10}$

Aha! compare K_a to K_b

$ClO^- + H_2O \rightleftharpoons HClO + OH^-$ (CB)

$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{3.5 \times 10^{-8}}$

$K_b = 2.9 \times 10^{-7}$

proof — Ans

Answer: K_b for ClO^- > K_a for NH_4^+ . Basic

b. KCNO

Setup:

$CNO^- + H_2O \rightleftharpoons HCNO + OH^-$ ← proof

(CB)

Answer: Basic ← Ans.

c. $Ni(ClO_4)_3$

Setup:

$Ni^{3+} + H_2O \rightleftharpoons NiOH^{2+} + H^+$ ∴ Acidic

or → $Ni(H_2O)_6^{3+} + H_2O \rightleftharpoons Ni(H_2O)_5OH^{2+} + H_3O^+$

ClO_4^- spectator ion

↓

$HClO_4$ = (SA)

Answer: Acidic

mol H+ = mol CH_3NH_2 at the equiv. pt.

PC

3. What is the pH at the equivalence point when 27.0 ml of 0.200 M CH_3NH_2 are titrated with 0.350 M HCl? SA

K_b for CH_3NH_2 is 4.4×10^{-4}.

Setup:

1st rxn

LR!

	H^+ calc	+	CH_3NH_2	→	$CH_3NH_3^+$
Before rxn	$.0154\,L \times .350\,\frac{mol}{L}$		$.0270\,L \times .200\,\frac{mol}{L}$		Ø
	$= 5.4 \times 10^{-3}$ mol		$= 5.40 \times 10^{-3}$ mol (same)		
Δ	-5.4×10^{-3}		-5.40×10^{-3}		$+5.40 \times 10^{-3}$
After rxn	Ø		Ø		5.40×10^{-3} mol $CH_3NH_3^+$

2nd Equilib

CA

$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$

	$CH_3NH_3^+$		CH_3NH_2	H_3O^+
I	$\frac{5.40 \times 10^{-3}\,mol}{(.0154 + .0270)\,L}$		Ø	Ø
C	$-x$		$+x$	$+x$
E	$.127 - x$		x	x

$$K_a\,CH_3NH_3^+ = \frac{K_w}{K_b\,CH_3NH_2} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$$

$$K_a = \frac{[CH_3NH_2]\,[H_3O^+]}{[CH_3NH_3^+]}$$

$$2.3 \times 10^{-11} = \frac{(x)\,(x)}{.127 - x \rightarrow \text{neg}}$$

Answer: 5.76

$[H_3O^+] = x = 1.7 \times 10^{-6}$

pH = 5.76

Approx

$.127 - x \approx .127$

$\frac{1.7 \times 10^{-6}}{.127}(100) < 5\%$

4. How many ml of 0.250 M HF (aq) must be added to 500.0 ml of ~~0.300 M NaF~~ to give a buffer of pH= 3.50? K_a for HF is 6.8×10^{-4}.

WA CB .300M F^-

Setup:

	HF	+ H_2O	$\rightleftharpoons$	F^-	+	H_3O^+
I	$\frac{Y\ mol}{Vol_{Total}}$			$\frac{(.500L)(.300\ mol/L)}{Vol_{Total}}$		∅
C	$-10^{-3.50}$			$+10^{-3.50}$		$+10^{-3.50}$
E	$\left(\frac{Y}{Vol_{Total}} - 10^{-3.50}\right)$			$\left(\frac{.15}{Vol_{Total}} + 10^{-3.50}\right)$		$(10^{-3.50})$

$$K_a = \frac{[F^-]\ [H_3O^+]}{[HF]}$$

$$6.8 \times 10^{-4} = \frac{(10^{-3.50})\ \left(\frac{.15}{Vol_{Total}} + \cancel{10^{-3.50}}\right)}{\left(\frac{Y}{Vol_{Total}} - \cancel{10^{-3.50}}\right)}$$

neg (numerator) neg (denominator)

Approx

$\frac{.15}{V_{Total}} + 10^{-3.50} \approx \frac{.15}{V_{Tot}}$

$\frac{Y}{V_{Total}} - 10^{-3.50} \approx \frac{Y}{V_{Tot}}$

$$6.8 \times 10^{-4} = \frac{(10^{-3.50})\ \left(\frac{.15}{Vol_{Total}}\right)}{\frac{Y}{Vol_{Total}}}$$

$$Y = .0706\ mol\ HF$$

$$mL\ HF = .0706\ mol\ HF \times \frac{1\ L}{.250\ mol\ HF}$$

Answer: 282 ml

= 282 mL of .250 M HF soln is added.

5. Find the pH of a solution made by mixing 25.0 ml of 0.0650 M benzylamine, $C_7H_7NH_2$, and 13.9 ml of 0.0500 M HCl. K_b for $C_7H_7NH_2$ is 4.7×10^{-10}

LR

Setup:

(A) HCl + (B) $C_7H_7NH_2$ → $C_7H_7NH_3^+$ +

Before: $.0139L \times .0500 \frac{mol}{L} = 6.95 \times 10^{-4}$ mol HCl; $.0250L \times .0650 \frac{mol}{L} = 1.63 \times 10^{-3}$ mol B; $\emptyset$; $+ 6.95 \times 10^{-4}$

$- 6.95 \times 10^{-4}$ mol HCl; $- 6.95 \times 10^{-4}$ mol B

After rxn: $\emptyset$; $.94 \times 10^{-3}$ mol $C_7H_7NH_2$ (B); 6.95×10^{-4} $C_7H_7NH_3^+$ (CA)

Equilibria

Method 1

	$C_7H_7NH_2$	+ H_2O ⇌	$C_7H_7NH_3^+$	+ OH^-	K_b
I	$\frac{.94 \times 10^{-3}}{(.0250 + .0139)L}$		$\frac{.695 \times 10^{-4}}{(.0250 + .0139)L}$	$\emptyset$	
C	$-x$		$+x$	$+x$	
E	$(2.4 \times 10^{-2} - x)$		$(1.79 \times 10^{-2} + x)$	(x)	

etc

$$K_b = \frac{[C_7H_7NH_3^+][OH^-]}{[C_7H_5NH_2]}$$

$$4.7 \times 10^{-10} = \frac{(1.79 \times 10^{-2} + x)(x)}{(2.4 \times 10^{-2} - x)}$$

Method 2

$$pH = pK_a + \frac{[A]}{[HA]}$$

$$= -\log \frac{K_w}{K_b} + \log \frac{(.94 \times 10^{-3})}{(6.95 \times 10^{-4})}$$

$$= 4.80$$

pH = 4.80

Answer: 4.80

6. A chemist wants to prepare a buffer of pH = 4.35. How many milliliters of 0.455 M acetic acid must be added to 465 ml of 0.0941 M NaOH solution to obtain such a buffer? Ka for $HC_2H_3O_2$ is 1.7×10^{-5}.

Setup:

1ST rxn

LR!

	$HC_2H_3O_2$	+	NaOH	→	$C_2H_3O_2^-$	+	H_2O
Before	C		$.465L \times .0941 \frac{mol}{L} = .0438\ mol$		∅		
Δ	$-.0438$		$-.0438$		$+.0438$		
After rxn	$C - .0438$ $C_2H_3O_2^-$		∅		$.0438$ mol $C_2H_3O_2^-$		

2nd Equilib.

	$HC_2H_3O_2$	+	H_2O	⇌	$C_2H_3O_2^-$	+	H_3O^+
I	$\frac{C - .0438}{V_{Total}}$				$\frac{.0438\ mol}{V_{Total}}$		∅
C	-4.5×10^{-5}				$+4.5 \times 10^{-5}$		$+4.5 \times 10^{-5}$
E	$\left(\frac{C - .0438}{V_{Total}} - 4.5 \times 10^{-5}\right)$				$\left(\frac{.0438}{V_{Total}} + 4.5 \times 10^{-5}\right)$		4.5×10^{-5}

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$= \frac{[4.5 \times 10^{-5}]\left(\frac{.0438}{V_{Total}} + 4.5 \times 10^{-5}\right)}{\left(\frac{C - .0438}{V_{Total}} - 4.5 \times 10^{-5}\right)}$$

neg

neg

Approx.

$\frac{.0438}{V} + 4.5 \times 10^{-5} \approx \frac{.0438}{V}$

$\frac{C - .0438}{V} - 4.5 \times 10^{-5} \approx \frac{C - .0438}{V}$

$$= \frac{(4.5 \times 10^{-5})\left(\frac{.0438}{V_{Total}}\right)}{\frac{C - .0438}{V_{Total}}}$$

$C = 0.160\ mol\ HC_2H_3O_2$ $V = .160\ mol \times \frac{1\ L}{4.55\ mol} = .351\ L$

Answer: 351 ml

7. a.

Setup:

$HC_2O_4^- + H^+ \rightarrow H_2C_2O_4$ (SA addition)

$HC_2O_4^- + OH^- \rightarrow H_2O + C_2O_4^{2-}$ (SB addition)

$HC_2O_4^-$

b. Is ~~$NaHC_2O_4$~~ (aq) acidic, basic, or neutral? K_{a1} for $H_2C_2O_4$ is 5.6×10^{-2}, K_{a2} for $HC_2O_4^-$ is 5.1×10^{-5}. You must show your work to justify your answer. Answer: Yes

Setup:

WA $HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$ $K_{a_2} = 5.1 \times 10^{-5}$

CB $HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$ $K_b = \frac{K_w}{K_{a_1} H_2C_2O_4}$

$= \frac{10^{-14}}{5.6 \times 10^{-2}}$

$= 1.8 \times 10^{-13}$

$K_a > K_b$

$5.1 \times 10^{-5} > 1.8 \times 10^{-13}$

∴ Acidic.

Answer: K_{a2} for $HC_2O_4^-$ > Kb for $HC_2O_4^-$, Acidic