C_3H_7COOH $(K_a = 1.5 \times 10^{-5})$

28. A solution is made by dissolving butanoic acid (aka "butyric acid") and sodium butanoate in water. The pH of this solution is then "adjusted" by adding nitric acid or sodium hydroxide.
a. Calculate the ratio of butanoate ion to butanoic acid in each case (pH value).
Show work for pH 3.82 and 4.82.

pH value:	2.82	3.82	4.82	5.82	6.82
ratio of [butanoate] / [butanoic acid]	0.010	0.10	1.0	10.	1.0×10^2 (100)

$$C_3H_7COOH \rightleftharpoons H^{+1} + C_3H_7COO^{-1}$$

$$K_a = \frac{[H^{+1}][C_3H_7COO^-]}{[C_3H_7COOH]} = 1.5 \times 10^{-5}$$

@ pH 3.824, $[H^+] = 10^{-3.824} = .00014997\,M$

$$\frac{(.00014997)[C_3H_7COO^-]}{[C_3H_7COOH]} = 1.5 \times 10^{-5} \quad \text{so} \quad \frac{[C_3H_7COO^-]}{[C_3H_7COOH]} = 0.10002 \to \boxed{0.10}$$

@ pH 4.824, $[H^+] = 10^{-4.824} = .00001499\,M$

$$\frac{(.00001499)[X^-]}{[HX]} = 1.5 \times 10^{-5}\,M$$

$$\frac{[X^-]}{[HX]} = 1.0002 \to \boxed{1.0}$$

b. What is the significance of value of 4.82 for this acid? Explain.

4.82 is the pKa of this acid, since $-\log(1.5 \times 10^{-5}) = 4.82(4)$

pH is equal to pKa when equal amounts of weak acid and conjugate base are present; when the ratio of $\frac{[X^-]}{[HX]} = 1.0$

29. A (very poisonous) solution is made by dissolving NaCN and HCN into water. The pH of this solution can then be "adjusted" by adding nitric acid or sodium hydroxide.
a. At what pH value will the concentrations of CN^{-1} and HCN be equal?

$[CN^-] = [HCN]$ when pH = pKa, so they'll be equal @ pH 9.31

$$\left(pKa(HCN) = -\log(K_a) = -\log(4.9 \times 10^{-10}) = 9.31 \right)$$

b. If the pH is adjusted to 9.0, how will the ratio of $[CN^{-1}]$ to [HCN] be affected? (relative to the ratio of 1, in part a)

If pH decreases below the pKa of 9.31, the solution is becoming more acidic, so [HCN] will increase, and [CN⁻] will decrease. So $\frac{[CN^-]}{[HCN]}$ will decrease to a value that is less than 1.0

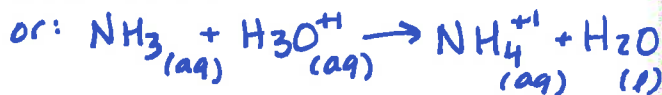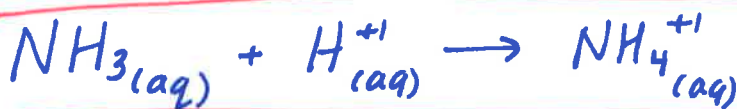**c.** Suppose that some silver nitrate is added to the solution. Silver nitrate is highly soluble into water, but silver cyanide is much less soluble. Will the AgCN precipitate be more likely to form at <u>high</u> pH or <u>low</u> pH (which one?). Explain your answer.

$$Ag^{+1}_{(aq)} + CN^{-1}_{(aq)} \rightleftharpoons AgCN_{(s)}$$
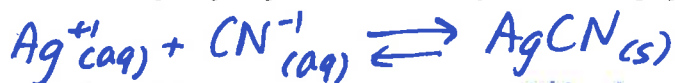
precipitation is more likely when [CN⁻] is relatively high.
[CN⁻] will increase as the solution becomes more basic,
so precipitation is more likely at high pH.

$NH_3 : K_b = 1.8 \times 10^{-5}$

30. A 50.0 mL solution of ammonia is titrated with HCl. 20.0 mL of 0.30 M HCl are required to reach the equivalence point. **a.** Write a chemical equation (net ionic) for the neutralization reaction that occurred.

$$NH_{3(aq)} + H^{+1}_{(aq)} \longrightarrow NH_4^{+1}{}_{(aq)}$$

or: $NH_{3(aq)} + H_3O^{+1}_{(aq)} \longrightarrow NH_4^{+1}{}_{(aq)} + H_2O_{(l)}$
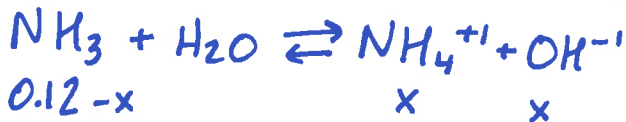
b. Calculate the molarity of the ammonia solution.

$$M_a V_a = M_b V_b$$

$$(0.30 M)(20.0 mL) = M_b (50.0 mL)$$

$$\boxed{M_b = 0.12 M}$$

c. Calculate the pH of the solution after 0, 10, 15, 20, and 25 mL HCl had been added to the solution of ammonia.

<u>0 mL:</u> no acid added, so we just have 0.12 M NH_3. Do a K_b.

$$NH_3 + H_2O \rightleftharpoons NH_4^{+1} + OH^{-1}$$
$$0.12 - x \qquad\qquad x \qquad x$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad 1.8 \times 10^{-5} = \frac{x^2}{.12 - x}$$

assume $x \ll 0.12$

$$1.8 \times 10^{-5} = \frac{x^2}{0.12}$$

$$x = [OH^-] = 0.0014(7) M$$

$(.010 L \, HCl)(.30 \frac{mol}{L}) = .0030$ moles HCl
$(.0500 L \, NH_3)(.12 \, mol/L) = .0060$ moles NH_3

$pH = 14 + log(OH^-) = \boxed{11.17}$

<u>10. mL:</u>

$$NH_3 + H^+ \longrightarrow NH_4^{+1}$$

I	.0060	.0030	0
Δ	-.0030	-.0030	+.0030
F	.0030	0	.0030

$[NH_3] = [NH_4^+] = \frac{.0030 \, mole}{.060 \, L} = 0.050 M$

Do K_b: $NH_3 + H_2O \rightleftharpoons NH_4^{+1} + OH^{-1}$
$\qquad\qquad .050 - x \qquad\qquad .050 + x \quad x$

once you get to this point, you could just say:
50/50 buffer, so $pOH = pK_b = -log(1.8 \times 10^{-5})$
so $pOH = 4.74$, $pH = 14 - 4.74 = 9.26$
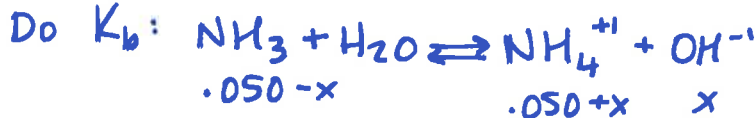
$K_b = \frac{(.050 + x)(x)}{(.050 - x)} = 1.8 \times 10^{-5}$

assume $x \ll .050$

$\frac{(.050)(x)}{(.050)} = 1.8 \times 10^{-5}$

$x = 1.8 \times 10^{-5}_M = [OH^-]$

$pOH = 4.74,$ $\boxed{pH = 9.26}$

<u>15 mL:</u> $NH_3 + H^{+1} \longrightarrow NH_4^{+1}$

.0060	.0045	0
-.0045	-.0045	+.0045
.0015	0	.0045

$[NH_3] = \frac{.0015 \, mole}{0.065 \, L} = 0.02308 M$

$[NH_4^+] = \frac{.0045 \, mole}{.065 \, L} = .069231 M$

Do K_b:

$$NH_3 + H_2O \rightleftharpoons NH_4^{+} + OH^{-1}$$
$$.02308 - x \qquad\qquad .069231 - x \quad x$$

$\frac{x(.069231 + x)}{(.02308 - x)} = 1.8 \times 10^{-5}$

$\frac{x(.0692)}{(.02308)} = 1.8 \times 10^{-5}$

assume $x \ll .023, .069$

$x = [OH^-] = 6.0 \times 10^{-6}_M$ $\boxed{pH = 8.78}$

(30c, continued)

20. mL:

$$NH_3 + H^{+1} \longrightarrow NH_4^{+1}$$

.0060	.0060	0
-.0060	-.0060	+.0060
0	0	.0060
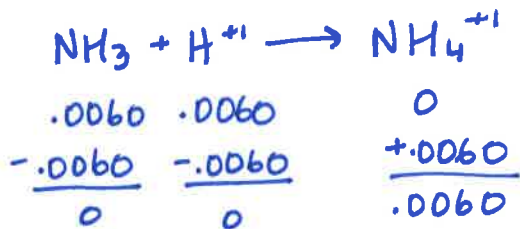
$$[NH_4^+] = \frac{.0060 \, mole}{.070 \, L} = 0.08571 \, M$$

equivalence point.. all NH_3 converted to NH_4^{+1}, a weak acid.

$$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_a: \quad NH_4^{+1} \rightleftharpoons H^{+1} + NH_3$$

$$\quad .08571-x \qquad x \qquad x$$

assume $x \ll .08571$
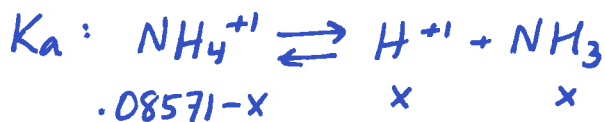
$$\frac{x^2}{.08571} = 5.56 \times 10^{-10}$$

$$K_a = \frac{x^2}{.08571-x} = 5.56 \times 10^{-10}$$

$$x = [H+] = 6.9 \times 10^{-6} M$$

$$\boxed{pH = 5.16}$$

25 mL: $\quad NH_3 + H^{+1} \longrightarrow NH_4^{+1}$

.0060	.0075	0
-.0060	-.0060	+.0060
0	.0015	.0060
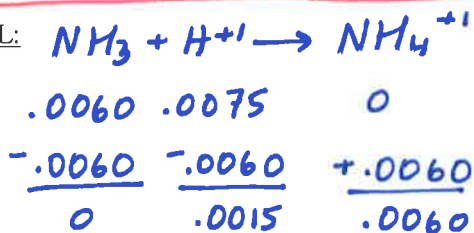
↑ strong acid

↑ weak acid (ignore)

← past the equivalence point.
all NH_3 converted to NH_4^{+1},
and excess HCl is present

$$[H+] = \frac{.0015 \, mole}{.075 \, L} = 0.020 \, M$$

$$pH = -\log(.020) = \boxed{1.70}$$

30d. Sketch a titration curve, including the 5 points calculated in part c.

pH vs. Volume of HCl (mL)
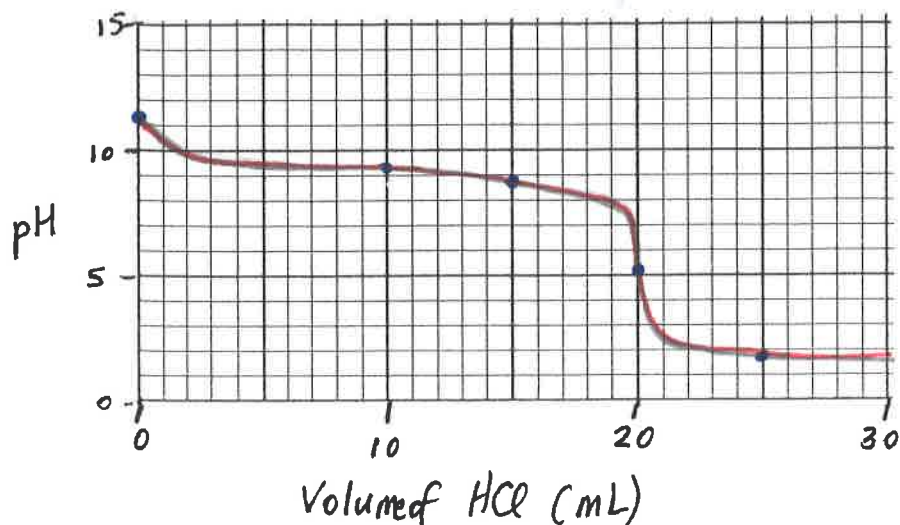
31. State whether the pH at the equivalence point will be acidic, basic, or neutral for each titration.

a. HBr titrated with NaOH __neutral__ (strong acid, strong base)

b. CH_3NH_2 titrated with HNO_3 __acidic__ (weak base, strong acid)

c. HNO_2 titrated with LiOH __basic__ (weak acid, strong base)

d. Cinnamic acid ($C_9H_8O_2$/C_8H_7COOH) titrated with $Ba(OH)_2$ __basic__ (weak acid, strong base)

e. ammonia titrated with HCl __acidic__ (weak base, strong acid)

f. NaOH titrated with $HClO_3$ __neutral__ (strong base, strong acid)

g. KNO_2 titrated with HCl __acidic__ (weak base, strong acid)
≈ (conj. base of HNO_2)

32. A solution of formic acid (methanoic acid) is titrated with potassium hydroxide.
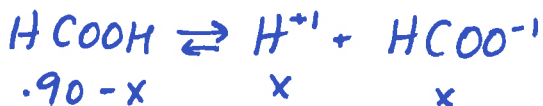30.0 mL of 0.90 M formic acid are titrated with 0.60 M KOH.

$HCOOH, K_a = 1.8 \times 10^{-4}$

a. What volume of KOH will be necessary to reach the equivalence point?

$$M_a V_a = M_b V_b \qquad (.90 M)(30.0 mL) = (0.60 M)V_b \qquad \boxed{V_b = 45 mL}$$

b. Calculate the pH of the solution when 0, 22.5, 40., 45, and 50. mL of KOH have been added.

0 mL KOH added: all we have is 0.90 formic acid, so do K_a calc.

$$HCOOH \rightleftharpoons H^{+1} + HCOO^{-1}$$
$$.90 - x \qquad x \qquad x$$

$$K_a = \frac{x^2}{.90 - x} = 1.8 \times 10^{-4}$$

assume $x << 0.90$

$$\frac{x^2}{.90} = 1.8 \times 10^{-4} \qquad x = .01273$$

→ this x value is a bit too large to "neglect" since it affects the second sig fig of .90

so, plug in: $\frac{x^2}{.90 - .01273} = 1.8 \times 10^{-4}$

$$x = .01264, \qquad [H^+] = .01264 M$$
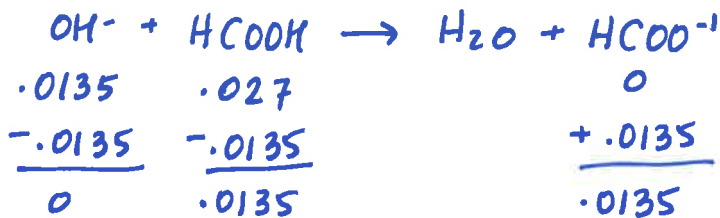$$x = .01264 \checkmark \qquad \boxed{pH = 1.90}$$

22.5 mL KOH added

$(.0225 L)(.60 M) = 0.0135 moles KOH$

$(.0300 L)(.90 M) = 0.027 moles HCOOH$

$$OH^- + HCOOH \longrightarrow H_2O + HCOO^{-1}$$

.0135	.027		0
-.0135	-.0135		+.0135
0	.0135		.0135

$[HCOOH] = [HCOO^-] = \frac{.0135 mole}{.0525 L} = 0.2571 M$

← we are halfway to the equivalence point, so half of the formic acid has reacted to form formate ion. So $[HCOOH] = [HCOO^{-1}]$

So we can say:
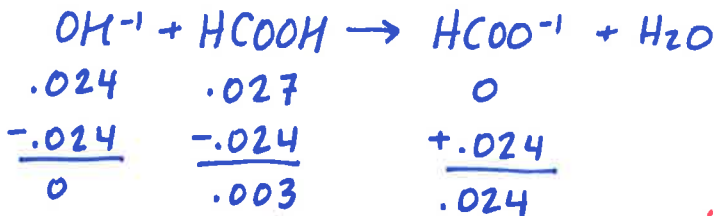50/50 buffer,

∴ $pH = pK_a = -\log(1.8 \times 10^{-4}) = \boxed{3.74}$

← or, we could use the molarities to do a K_a calculation and get the same result!

$(.0400 L)(.60 \frac{mol}{L}) = .024$ moles
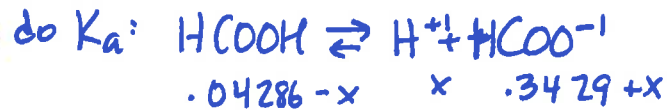
40.0 mL KOH added:

$$OH^{-1} + HCOOH \longrightarrow HCOO^{-1} + H_2O$$

.024	.027	0
-.024	-.024	+.024
0	.003	.024

$[HCOOH] = .003$ mole$/.070$ L $= .04$(286) M   ← ISF

$[HCOO^-] = .024$ mole$/.070$ L $= .3429$ M

do K_a: $HCOOH \rightleftharpoons H^{+1} + HCOO^{-1}$

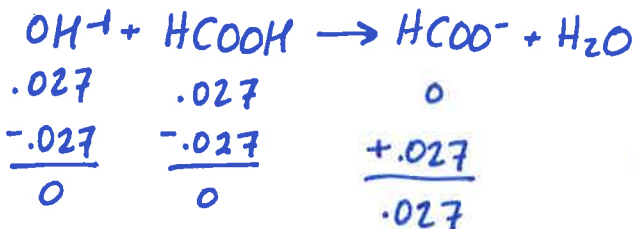|		
$.04286 - x$	x	$.3429 + x$

$$K_a = \frac{x(.3429 + x)}{.04286 - x} = 1.8 \times 10^{-4}$$

ass. $x \ll .043, .34$

$$\frac{x(.3429)}{.04286} = 1.8 \times 10^{-4} \qquad x = 2.25 \times 10^{-5} M$$
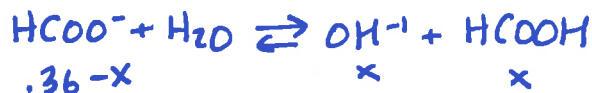
$$pH = -\log(2.25 \times 10^{-5}) = \boxed{4.6}$$

45.0 mL KOH added:

$$OH^{-1} + HCOOH \longrightarrow HCOO^- + H_2O$$

.027	.027	0
-.027	-.027	+.027
0	0	.027

$[HCOO^-] = 0.027$ mole$/.075$ L $= 0.36$ M

we are at the equivalence pt, so all the formic acid has been converted to formate ion. do K_b with formate.

$$K_b (HCOO^-) = \frac{K_w}{K_a(HCOOH)} = \frac{10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$HCOO^- + H_2O \rightleftharpoons OH^{-1} + HCOOH$$
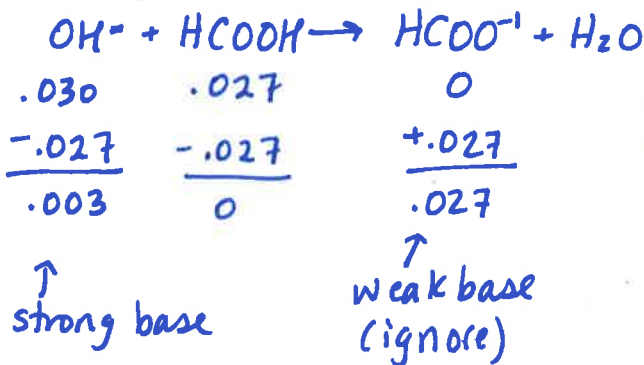
$.36 - x$	x	x

$$K_b = \frac{x^2}{.36 - x} = 5.56 \times 10^{-11}$$

assume $x \ll .36$

$$\frac{x^2}{.36} = 5.56 \times 10^{-11}$$

$$x = [OH^-] = 4.47 \times 10^{-6} M$$

$$\boxed{pH = 8.65}$$

50.0 mL KOH added:

$$OH^- + HCOOH \longrightarrow HCOO^{-1} + H_2O$$

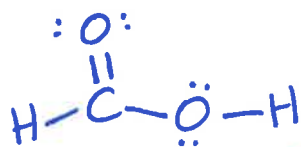|		
.030	.027	0
-.027	-.027	+.027
.003	0	.027

↑ strong base

↑ weak base (ignore)

we are past the equiv. pt. so all the formic acid has been converted to formate ion, and excess KOH is present.
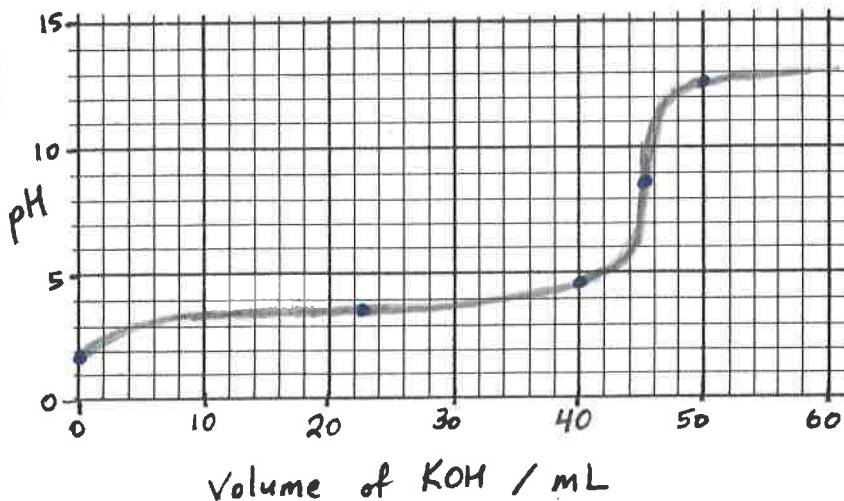
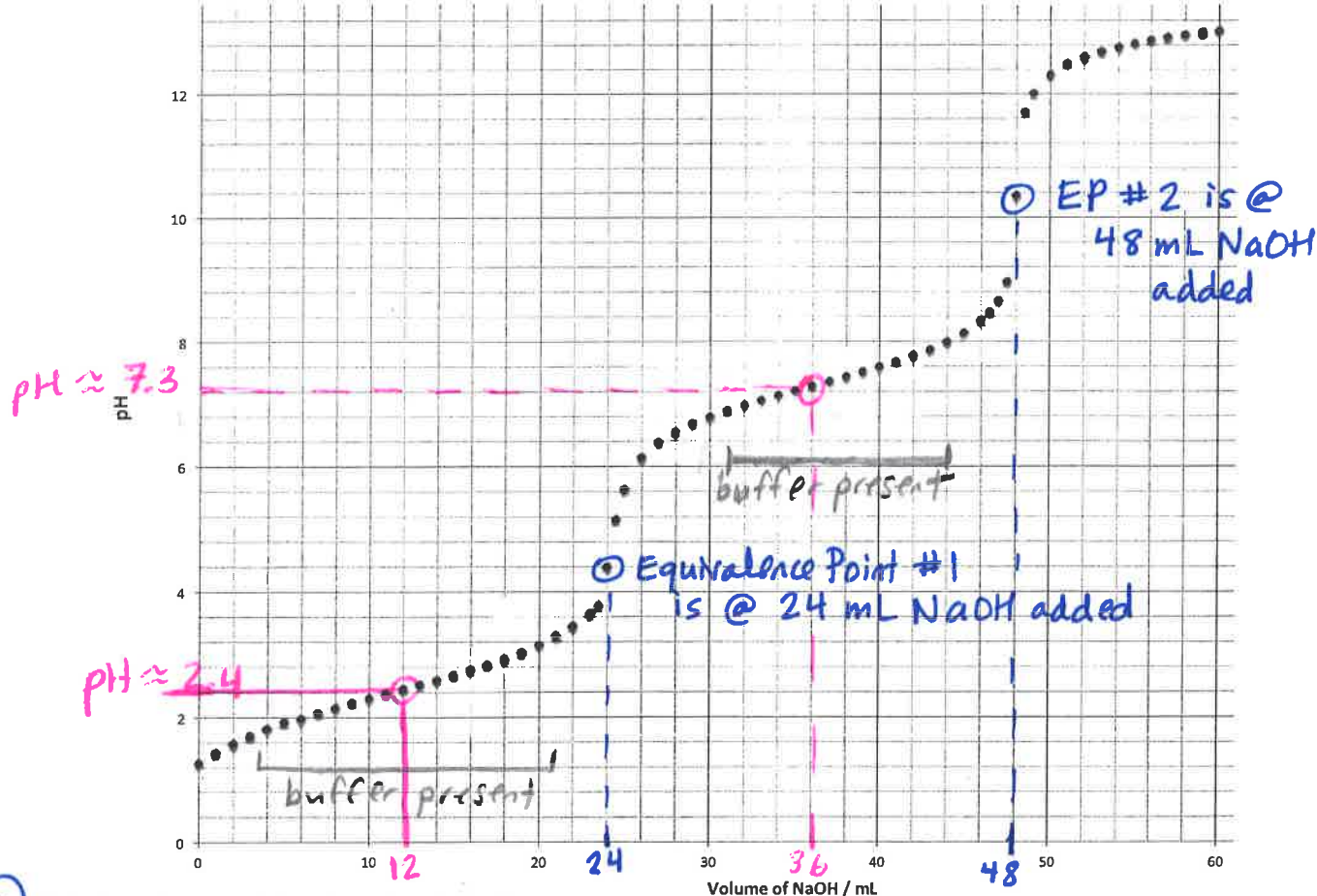$$[OH^-] = \frac{.003 \text{ mole}}{.080 L} = .0375 M$$

$$pH = 14 + \log(.0375) = \boxed{12.6}$$

c. Sketch a graph of the titration curve, including the 5 points calculated in part (b).

Formic (methanoic) acid

$$H - \overset{\overset{\displaystyle :O:}{\|}}{C} - \overset{..}{\underset{..}{O}} - H$$

↑ acidic hydrogen

Volume of KOH / mL

pH ≈ 7.3

⊙ EP #2 is @ 48 mL NaOH added

buffer present

⊙ Equivalence Point #1 is @ 24 mL NaOH added

pH ≈ 2.4

buffer present

12   24   36   48

Volume of NaOH / mL

33. H_2SeO_3 (selenous acid) is titrated with NaOH.
20.0 mL of 0.88 M H_2SeO_3 are titrated with a solution of NaOH, and the above titration curve is obtained:

a. Write the net ionic equation for the first neutralization rxn that occurs (include subscripts).

$$H_2SeO_{3(aq)} + OH^{-1}_{(aq)} \longrightarrow H_2O_{(\ell)} + HSeO_3^{-1}{}_{(aq)}$$

b. Write the net ionic equation for the second neutralization rxn that occurs (include subscripts).

$$HSeO_3^{-1}{}_{(aq)} + OH^{-1}_{(aq)} \longrightarrow H_2O_{(\ell)} + SeO_3^{-2}{}_{(aq)}$$

c. Calculate the molarity of the NaOH solution.

Based on graph,
EP #1 is at 24 mL,
and EP #2 is at 48 mL.

using EP #1: $M_aV_a = M_bV_b$

$$(0.88\ M)(20.0\ mL) = M_b(24\ mL)$$

$$M_b = 0.733 \rightarrow \boxed{0.73\ M}$$

d. Determine pK_{a1} and K_{a1} of selenous acid.

$\dfrac{24\ mL}{2} = 12\ mL$ pH @ 12 mL ≈ 2.4, acc to graph.

12 mL is halfway to the equivalence point, so half of the H_2SeO_3 has been converted to $HSeO_3^{-1}$, so $[H_2SeO_3] = [HSeO_3^{-1}]$, so $pH = pK_{a1}$

so $\boxed{pK_{a1} = 2.4}$ $\boxed{K_{a1} = 10^{-2.4} = 0.004}$

#33, Cont'd !

e. Determine pK_{a2} and K_{a2} of selenous acid. at 36 mL, $pH \approx 7.3$ acc to graph.

Read pH @ 36 mL, since 36 mL is halfway between EP#1 and EP#2, so half of the $HSeO_3^{-1}$ (present @ EP#1) remains, and half has been converted to SeO_3^{-2}, so $[HSeO_3^-] = [SeO_3^{-2}]$, so $pH = pKa_2$ of H_2SeO_3.
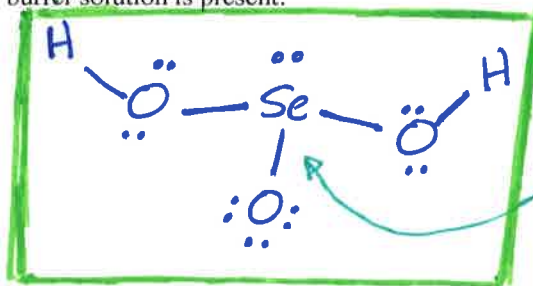
$$\boxed{pKa_2 = 7.3}$$

$$Ka_2 = 10^{-7.3} = 5.01 \times 10^{-8} \rightarrow \boxed{Ka_2 = 5 \times 10^{-8}}$$

f. Label the regions on the titration curve where a buffer solution is present.

Done - see previous page.

g. Draw the Lewis Dot structure of selenous acid.

H_2SeO_3 : 26 valence electrons

this bond could have some double bond character, since this would give formal charges closer to zero.

For the rest of this problem, use the book values for Ka1 and Ka2: Ka1 = 0.0035, and Ka2 = **5.0**x 10^{-8}.
(these may not match the values in your book..)

$pKa_1 = 2.46, pKa_2 = 7.30$

h. Suppose that you have solutions of H_2SeO_3, $KHSeO_3$, and K_2SeO_3.
If you need to make a buffer with a pH of 7.90. Which two compounds should you use?

use $\boxed{KHSeO_3 \text{ and } K_2SeO_3}$. (these contain $HSeO_3^{-1}$ and SeO_3^{-2} ions)

We need to use an acid with a pka near 7.90.

pKa_2 of H_2SeO_3 is 7.30, or, in other words, Ka of $HSeO_3^{-1}$ is 7.30. So the acid needs to be $HSeO_3^{-1}$, and the conjugate base will be SeO_3^{-2}

i. What are possible values for the molarities of the two compounds in your buffer solution? (in part h)
(Find one possible set of molarities; many answers are possible).

$$HSeO_3^{-1} \rightleftharpoons H^{+1} + SeO_3^{-2}$$

$$Ka = \frac{[H^+][SeO_3^{-2}]}{[HSeO_3^{-1}]} = 5.0 \times 10^{-8}$$

$$\frac{(10^{-7.90})[SeO_3^{-2}]}{[HSeO_3^-]} = 5.0 \times 10^{-8}$$

$$\frac{(1.2589 \times 10^{-8}M)[SeO_3^{-2}]}{[HSeO_3^-]} = 5.0 \times 10^{-8}$$

$$\frac{[SeO_3^{-2}]}{[HSeO_3^-]} = 3.97$$

So, I'll use these :

0.10 M $HSeO_3^{-1}$
and 0.397 M SeO_3^{-2}

$\boxed{0.10 \ M \ KHSeO_3 \\ 0.397 \ M \ K_2SeO_3}$

pH > pKa so it makes sense that there is more base than acid present in buffer.

or larger / smaller molarities — must be related by factor of 3.97!

(0, 9.45)

(15, 5.4)

(18.5, 5.23)

← equivalence pt at 37 mL HCl

(45, 1.28)

pH vs Volume of HCl / mL
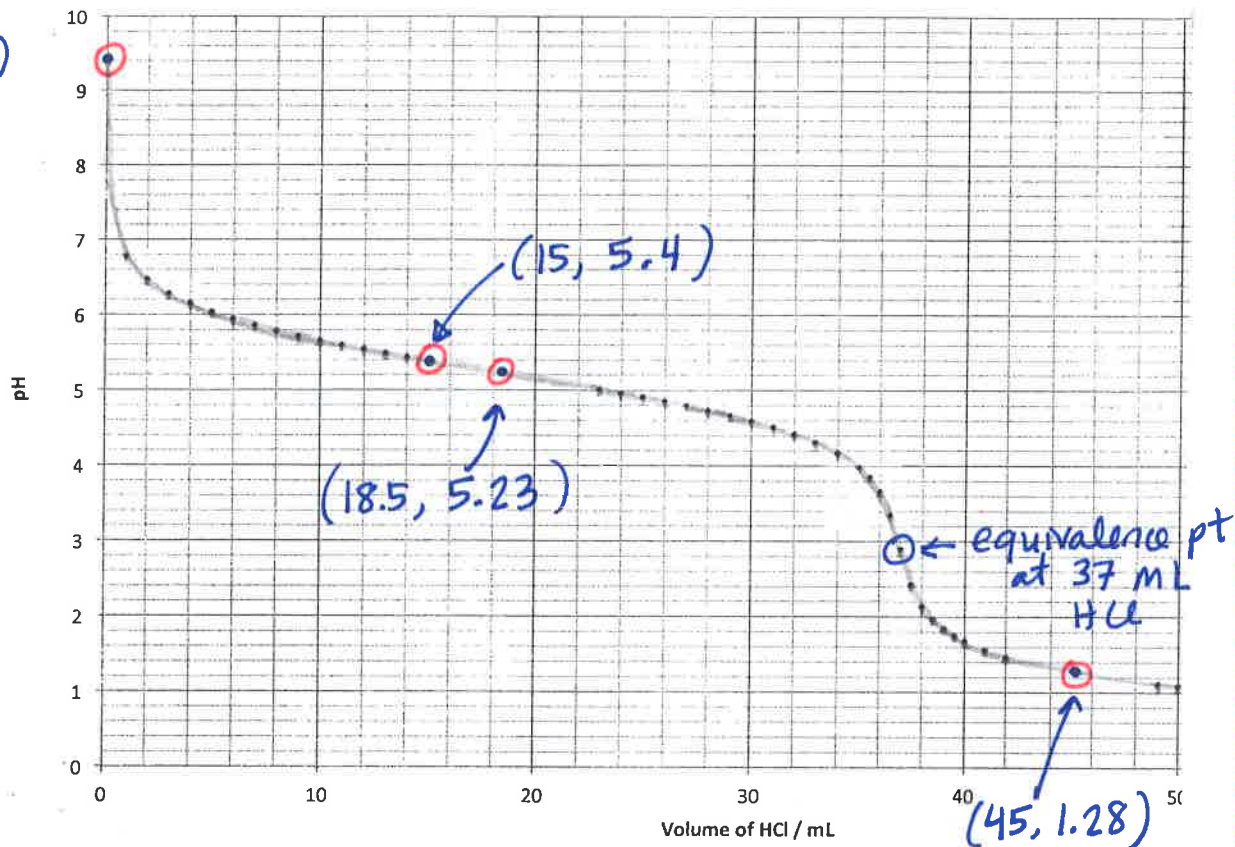
34. An organic base is titrated with HCl. 1.84 grams of the organic base are dissolved into water, to make 50.0 mL of solution. The base is then titrated with 0.629 Molar HCl to obtain the (partial) titration curve shown above.

a. Calculate the moles of the organic base initially present.

acc to graph, 37 mL HCl needed to reach the equivalence point.

$(.037 \text{ L } HCl)\left(\dfrac{0.629 \text{ mole}}{L}\right)\left(\dfrac{1 \text{ mole organic base}}{1 \text{ mole } HCl}\right) = 0.02327$ moles organic base were present

→ **0.023 moles**

b. Calculate molar mass of the organic base.

$\dfrac{1.84 g}{0.02327 \text{ moles}} = 79.06 \rightarrow$ **79 g/mole**

c. The organic base is one of these:

aniline ($C_6H_5NH_2$; $Kb = 4.3 \times 10^{-10}$) 93 amu
pyridine (C_5H_5N; $Kb = 1.7 \times 10^{-9}$) 79 amu
imidazole ($C_3H_4N_2$; $Kb = 9.1 \times 10^{-8}$) 68 amu
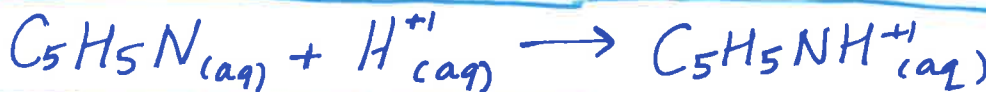
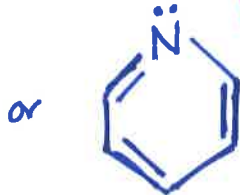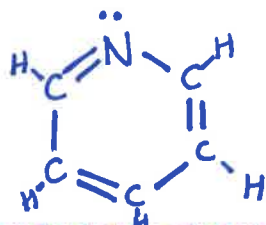Identify the base, based on the molar mass you determined in part (b). pyridine! C_5H_5N!

d. Write the hydrolysis reaction that occurs between the organic base and water. (the reaction that corresponds to Kb)
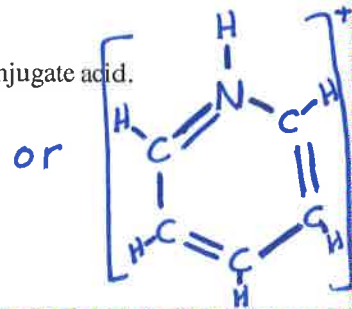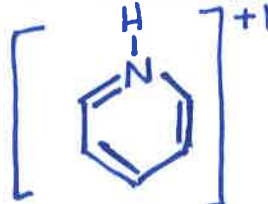
$$C_5H_5N_{(aq)} + H_2O_{(l)} \rightleftarrows C_5H_5NH^{+1}_{(aq)} + OH^{-1}_{(aq)}$$

e. Write the neutralization reaction that occurs between the organic base and the HCl (net ionic).

$$C_5H_5N_{(aq)} + H^{+1}_{(aq)} \longrightarrow C_5H_5NH^{+1}_{(aq)}$$

f. Draw the Lewis Dot structure of the base.   **g.** Draw the Lewis Dot structure of the base's conjugate acid.

#34, cont'd !

h. Calculate the pH of the solution at the following points in the titration: (use this for next two volumes from part (a))

0 mL HCl added: start of titration : 0.023(27) moles pyridine present, in 50.0 mL.

$$[C_5H_5N] = \frac{0.02327\ moles}{0.0500\ L} = 0.46546\ M \rightarrow 0.47\ M$$

Do K_b:

$$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^{+1} + OH^{-1}$$

0.46546−x   x   x

$$K_b = \frac{x^2}{0.46546-x} = 1.7\times10^{-9}\quad ass.\ x \ll .465$$

$$\frac{x^2}{.46546} = 1.7\times10^{-9}$$

$$x = [OH^-] = 2.8\times10^{-5}\ M$$

$$\boxed{pH = 9.45}$$

15 mL HCl added

$$(0.015\ L)(0.629\ \tfrac{mole}{L}) = 0.009435\ moles\ HCl$$
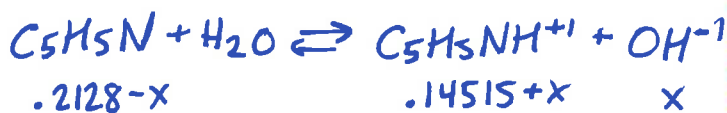
$$H^{+1} + C_5H_5N \longrightarrow C_5H_5NH^{+1}$$

.009435   .02327   0

−.009435   −.009435   +.009435

0   0.01384 moles   .009435 moles

$$[C_5H_5N] = \frac{0.01384\ mole}{0.065\ L} = 0.2128\ M$$

$$[C_5H_5NH^{+1}] = \frac{.009435\ mole}{.065\ L} = 0.14515\ M$$

→ now do K_b (or K_a using $C_5H_5NH^+$)

$$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^{+1} + OH^{-1}$$

.2128−x   .14515+x   x

$$K_b = \frac{(.14515+x)x}{(.2128-x)} = 1.7\times10^{-9}$$

ass. $x \ll .145, .2128$

$$\frac{(.14515)x}{.2128} = 1.7\times10^{-9}$$

$$x = [OH^-] = 2.49\times10^{-9}\ M$$

$$\boxed{pH = 5.40}$$

45 mL HCl added (this is past the EP)

$$(.045\ L)(.629\ \tfrac{mole}{L}) = 0.028305\ moles\ HCl$$

$$H^{+1} + C_5H_5N \longrightarrow C_5H_5NH^{+1}$$

.028305   .02327   0

−.02327   −.02327   +.02327

.00504   0   .02327

↳ strong acid. use this to find pH.   ↳ weak acid (ignore)

$$[H^+] = \frac{.00504\ moles}{0.095\ L} = 0.053\ M$$

$$pH = -\log(.053) = \boxed{1.28}$$

18.5 mL of HCl added (for the this one, do the volume at which a 50/50 buffer exists!)

EP volume of 37 mL divided by 2 = 18.5 mL

at 18.5 mL, $[C_5H_5N] = [C_5H_5NH^{+1}]$

50/50 buffer so $pOH = pK_b = -\log(1.7\times10^{-9}) = 8.77$, so $\boxed{pH = 5.23}$

i. Plot the above 4 points on the graph on the previous page.

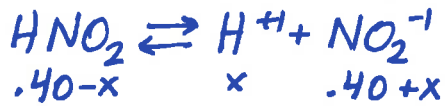or $pH = pK_a = -\log\left(\frac{10^{-14}}{1.7\times10^{-9}}\right) = 5.23$

where $\left(\frac{10^{-14}}{1.7\times10^{-9}}\right)$ is the K_a of $C_5H_5NH^+$

$$K_a = 4.5 \times 10^{-4} \rightarrow HNO_2 \qquad\qquad NaNO_2$$

35. A buffer solution was created by mixing 200. mL of 0.80 M nitrous acid with 200. mL of 0.80 M sodium nitrite.

a. Find the pH of this solution.

after mixing, total V will be 400. mL
the molarities will drop to 0.40 M

$$HNO_2 \rightleftarrows H^{+1} + NO_2^{-1}$$
$$.40-x \qquad x \qquad .40+x$$

$$K_a = \frac{x(.40+x)}{(.40-x)} = 4.5 \times 10^{-4}$$

assume $x \ll 0.40$

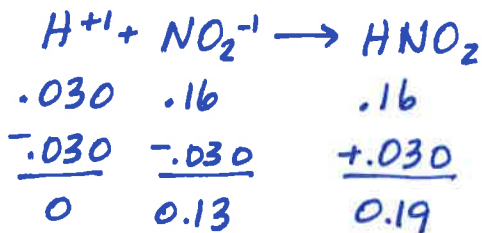$$\frac{x(.40)}{(.40)} = 4.5 \times 10^{-4}$$

$$x = [H^+] = 4.5 \times 10^{-4}$$
$$pH = -\log(4.5 \times 10^{-4}) = 3.35$$

OR: since $[HNO_2] = [NO_2^-]$,
it is a "50/50 buffer"
so $pH = pK_a$
so $pH = -\log(4.5 \times 10^{-4})$
$$= 3.35$$

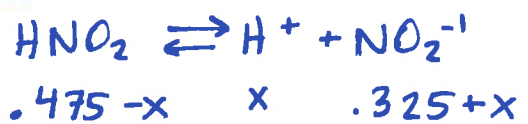**b.** Find the pH if 0.030 moles of HCl are added to this buffer solution. Assume that the volume change is negligible.

$$(.200L)(.80 \tfrac{mole}{L}) = 0.16 \text{ moles of } HNO_2 \text{ and of } NO_2^{-1} \text{ initially}$$

$$H^{+1} + NO_2^{-1} \longrightarrow HNO_2$$
$$.030 \quad .16 \qquad\qquad .16$$
$$\underline{-.030 \quad -.030 \qquad +.030}$$
$$0 \qquad 0.13 \qquad\qquad 0.19$$

neutralize the added HCl (H+) by reacting it with NO_2^{-1}

$$[NO_2^-] = \frac{.13 \, mole}{.400 L} = 0.325 \, M$$

$$[HNO_2] = \frac{.19 \, mole}{.400 L} = 0.475 \, M$$

use these to do K_a:

$$HNO_2 \rightleftarrows H^+ + NO_2^{-1}$$
$$.475-x \qquad x \qquad .325+x$$

$$K_a = \frac{x(.325+x)}{(.475-x)} = 4.5 \times 10^{-4}$$

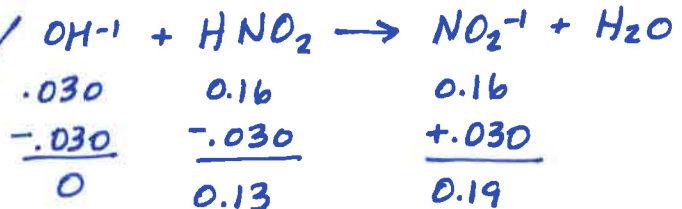assume $x \ll .325, .475$

$$\frac{x(.325)}{.475} = 4.5 \times 10^{-4} \qquad x = [H^+] = .000658 \, M$$

$$pH = 3.18$$

c. Find the pH if 0.030 moles of KOH are added to this buffer solution. Assume that the volume change is negligible.
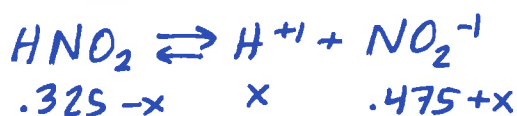
first, neutralize the added KOH by reacting it with $HNO_2 \rightarrow$

$$OH^{-1} + HNO_2 \longrightarrow NO_2^{-1} + H_2O$$
$$.030 \qquad 0.16 \qquad\qquad 0.16$$
$$\underline{-.030 \qquad -.030 \qquad +.030}$$
$$0 \qquad 0.13 \qquad\qquad 0.19$$

$$[HNO_2] = .13 \, mole / .400L = 0.325 \, M$$
$$[NO_2^-] = .19 \, mole / .400L = 0.475 \, M$$

now do a K_a calc:

$$HNO_2 \rightleftarrows H^{+1} + NO_2^{-1}$$
$$.325-x \qquad x \qquad .475+x$$

$$K_a = \frac{x(.475+x)}{(.325-x)} = 4.5 \times 10^{-4}$$

ass. $x \ll .475, .325$

$$\frac{x(.475)}{(.325)} = 4.5 \times 10^{-4} \qquad (.0003079)$$

$$x = [H^+] = .00031 \, M$$
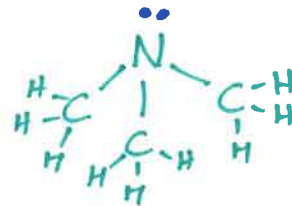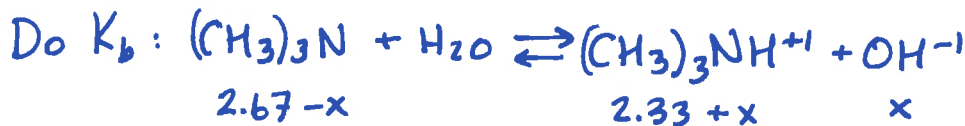$$pH = -\log(.00031) = 3.51$$

36. A buffer solution with a volume of 300. mL contains 0.80 moles of trimethylamine, and 0.70 moles of trimethylammonium chloride.

a. Find the pH of this solution. K_b of $(CH_3)_3N = 6.4 \times 10^{-5}$

$$[(CH_3)_3N] = \frac{.80 \text{ mole}}{.300 L} = 2.67 \text{ M} \qquad [(CH_3)_3NH^+] = \frac{.70 \text{ mole}}{.300 L} = 2.33 \text{ M}$$

Do K_b: $(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^{+1} + OH^{-1}$

$2.67 - x \qquad\qquad 2.33 + x \qquad\quad x$

$$K_b = \frac{(2.33+x)(x)}{(2.67-x)} = 6.4 \times 10^{-5} \qquad \frac{(2.33)x}{(2.67)} = 6.4 \times 10^{-5} \qquad x = [OH^-] = 7.31 \times 10^{-5} M$$
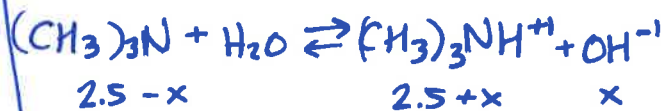
ass. $x \ll 2.33, 2.67$

$pOH = 4.14$

$\boxed{pH = 9.86}$

b. Find the pH if 0.050 moles of HCl are added to this buffer solution. Assume that the volume change is negligible.

first, neutralize the added HCl by reacting it with the base (trimethylamine)

$H^{+1} + (CH_3)_3N \longrightarrow (CH_3)_3NH^{+1}$

.050 mole	.80 mole	.70 mole
-.050	-.050	+.050
0	0.75	0.75

$[(CH_3)_3N] = [(CH_3)_3NH^+] = \frac{0.75 \text{ mole}}{.300 L} = 2.5 \text{ M}$

(at this point you could just do the shortcut and say 50/50 buffer ∴ $pOH = pK_b = -\log(6.4 \times 10^{-5}) = 4.19$, so $pH = 9.81$)
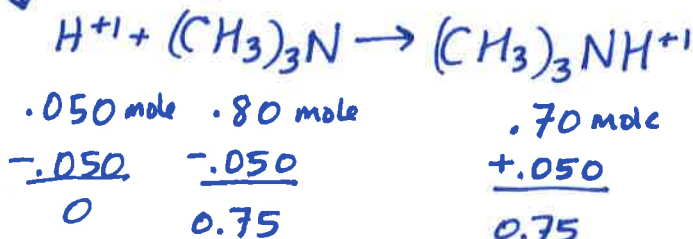
→ Now do a K_b calculation (unless you just do the shortcut at bottom!)

$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^{+1} + OH^{-1}$

$2.5 - x \qquad\qquad 2.5 + x \qquad\quad x$

$$K_b = \frac{(2.5+x)(x)}{(2.5-x)} = 6.4 \times 10^{-5}$$

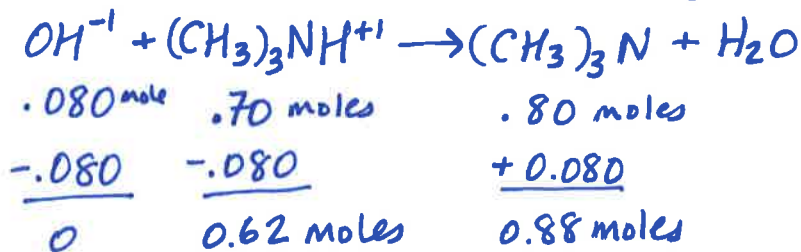ass. $x \ll 2.5 \qquad \frac{2.5(x)}{2.5} = 6.4 \times 10^{-5}$

$x = [OH^-] = 6.4 \times 10^{-5} M$, $\boxed{pH = 9.81}$

c. Find the pH if 0.080 moles of KOH are added to this buffer solution. Assume that the volume change is negligible.

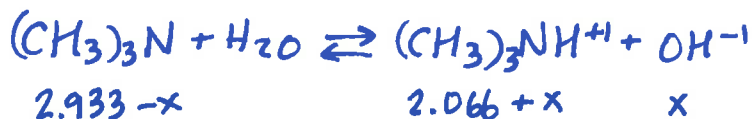first, neutralize the added KOH by reacting it with the acid: trimethylammonium ion :

$OH^{-1} + (CH_3)_3NH^{+1} \longrightarrow (CH_3)_3N + H_2O$

.080 mole	.70 moles	.80 moles
-.080	-.080	+0.080
0	0.62 moles	0.88 moles

$[(CH_3)_3NH^+] = \frac{.62 \text{ mole}}{.300 L} = 2.066 \text{ M}$

$[(CH_3)_3N] = \frac{.88 \text{ mole}}{.300 L} = 2.933 \text{ M}$

then do a K_b (or you could do K_a for part a, b, or c at this point instead)

$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^{+1} + OH^{-1}$

$2.933 - x \qquad\qquad 2.066 + x \qquad\quad x$

$$K_b = \frac{(2.066+x)x}{2.933-x} = 6.4 \times 10^{-5}$$

ass. $x \ll 2.06, 2.93$

$$\frac{(2.066)x}{(2.933)} = 6.4 \times 10^{-5}$$

$x = [OH^-] = 9.09 \times 10^{-5} M$

$\boxed{pH = 9.96}$