AP Acid Base Review January 2018 Answer Key!

**Problems for Test Review:**

$H_2CO_3$: Ka1 = 4.3 x $10^{-7}$, Ka2 = 5.6 x $10^{-11}$
$H_2SO_3$: Ka1 = 0.015, Ka2 = 6.4 x $10^{-8}$
$H_3PO_4$: Ka1 = 0.0075, Ka2 = 6.2 x $10^{-8}$, Ka3 = 4.2 x $10^{-13}$

Hypobromous acid, HBrO: Ka = 2.5 x $10^{-9}$
Trimethyl amine, $(CH_3)_3N$: Kb = 6.4 x $10^{-5}$
$Ag_2CO_3$: Ksp = 8.1 x $10^{-12}$

**1.** A buffer contains trimethyl amine $(CH_3)_3N$, dissolved at 0.20 M, and trimethyl ammonium chloride $((CH_3)_3NHCl)$, dissolved at 0.22 M.
a. Find the pH of the buffer.
b. Find pH if 0.004 moles of NaOH are added to 200. mL of the buffer. (assume no volume change)
c. Find pH if 0.004 moles of HCl are added to 200. mL of the buffer. (assume no volume change)

$K_b$ rxn:

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

0.20 - X          0.22 + X          X

assume x << .20, .22

$\dfrac{.22(x)}{.20} = 6.4 \times 10^{-5}$
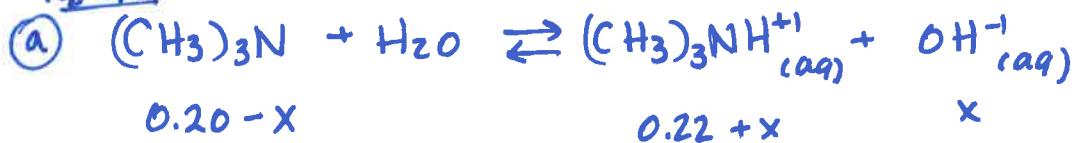
$K_b = \dfrac{[(CH_3)_3NH^{+}][OH^-]}{[(CH_3)_3N]} = \dfrac{(0.22+x)(x)}{0.20-x} = 6.4 \times 10^{-5}$

x = [OH⁻] = 5.818 × $10^{-5}$

pOH = 4.24

**pH = 9.76**

→ first neutralize any strong base or acid present

(b) $OH^- + (CH_3)_3NH^{+1} \rightleftharpoons (CH_3)_3N + H_2O$
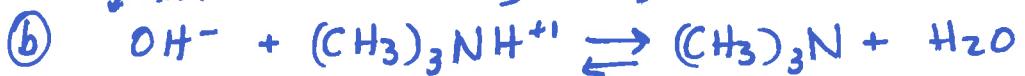
.004 moles    .044 moles         .040 moles
-.004 moles   -.004 moles        +.004 moles
   0          .040 moles         .044 moles

$[(CH_3)_3NH^+] = \dfrac{.040 \, mole}{0.200L} = 0.20M$

$[(CH_3)_3N] = \dfrac{.044 \, mol}{.200L} = 0.22M$

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

.22 - X          .20 + x          X
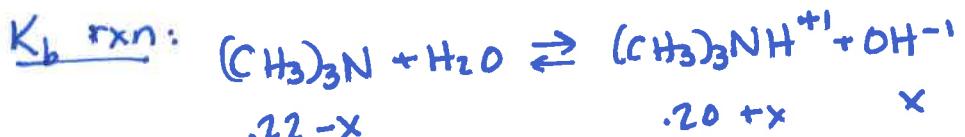
$K_b = \dfrac{x(.20+x)}{(.22-x)} = 6.4 \times 10^{-5}$

ass. x << .22, .20

x = [OH⁻] = .0000704 M
pOH = 4.15

**pH = 9.85**

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

.004      .040          .044
-.004    -.004         +.004
  0      .036          .048

$\dfrac{.036}{.200L} = 0.18M$

$\dfrac{.048}{.200L} = 0.24M$

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

.18 - X          .24 + X          X

$K_b = \dfrac{x(.24+x)}{(.18-x)} = 6.4 \times 10^{-5}$

ass. x << .18, .24

$\dfrac{x(.24)}{.18} = 6.4 \times 10^{-5}$

x = [OH⁻] = 4.8×$10^{-5}$

**pH = 9.68**

**2.** Determine the pH of

**a.** 0.040 M KOH   *strong base*

$$pOH = -\log(.040\,M) = 1.398 \qquad pH = 14 - 1.398 = 12.602 \rightarrow \boxed{12.60}$$

**b.** 0.040 M Ba(OH)₂   *strong base*

$[Ba^{+2}] = .040\,M$
$[OH^-] = 0.080\,M$

$$pOH = -\log(.080) = 1.0969 \qquad pH = 12.903 \rightarrow \boxed{12.90}$$

**c.** 0.040 M LiBr

$\boxed{pH = 7.00}$   since LiBr is neutral.

$Li^{+1} = IA = neutral$
$Br^{-1} = conj.\ base\ of\ HBr\ (strong)$
   $so\ Br^{-1} = neutral$

**d.** 0.040 M HBr   *strong acid.* $[H^+] = .040\,M$

$$pH = -\log(.040) = \boxed{1.40}$$

**e.** 0.040 M NaH   *strong base*

$NaH + H_2O \rightarrow NaOH + H_2(g)$   so $[OH^-] = .040\,M$

$H^{-1}_{(aq)} + H_2O \rightarrow OH^{-1} + H_2(g)$

$$pH = 14 + \log(.040) = \boxed{12.60}$$

**f.** A solution was made by dissolving 0.040 moles of K₂O into water, so that total solution volume is 300. mL

$\dfrac{.040\ moles}{0.300\ L} = 0.13\overline{3}\ M\ K_2O$   (strong base)

$[OH^-] = 2(.13\overline{3}) = 0.26\overline{6}\ M$

$$pH = 14 + \log(.26\overline{6}) = \boxed{13.43}$$

$K_2O + H_2O \rightarrow 2KOH$
$O^{-2} + H_2O \rightarrow 2OH^-$
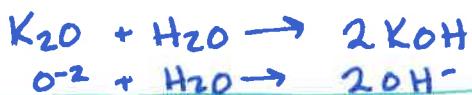
**g.** 0.10 M HBrO

weak acid. Look up $K_a : 2.5\times10^{-9}$

$HBrO \rightleftharpoons H^{+1} + BrO^{-1}$
   $.10-x \qquad x \qquad x$

$K_a = \dfrac{x^2}{.10-x} = 2.5\times10^{-9}$

ass. $x \ll .10$

$\dfrac{x^2}{.10} = 2.5\times10^{-9}$

$x = [H^+] = 1.58\times10^{-5}\ M$

$\boxed{pH = 4.80}$

**h.** 0.10 M KBrO

$K^{+1} / BrO^{-1}$ (weak base)

$BrO^{-1} + H_2O \rightleftharpoons OH^{-1}_{(aq)} + HBrO$
   $.10-x \qquad x \qquad x$
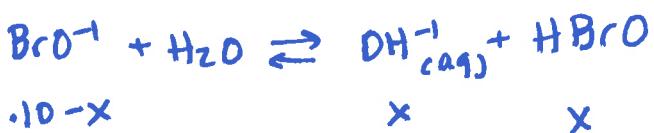
$K_b = \dfrac{x^2}{.10-x} = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{2.5\times10^{-9}} = 4.0\times10^{-6}$

ass. $x \ll .10$

$\dfrac{x^2}{.10} = 4.0\times10^{-6}$

$x = [OH^-] = 0.00063(2)\ M$

$\boxed{pH = 10.80}$

#2, cont'd

$[HBrO] = [BrO^{-1}]$

i. A solution where the concentration of HBrO and KBrO are equal.

50/50 buffer

$\therefore pH = pKa = -\log(2.5\times10^{-9}) = \boxed{8.60}$

---

j. A solution where [HBrO] = 0.20 M, and [NaBrO] = 0.10 M

$HBrO \rightleftharpoons H^{+1} + BrO^{-1}$

$.20 - x \qquad x \qquad .10 + x$

$Ka = \dfrac{x(.10 + x)}{.20 - x} = 2.5\times10^{-9}$

ass. $x \ll .10, .20$
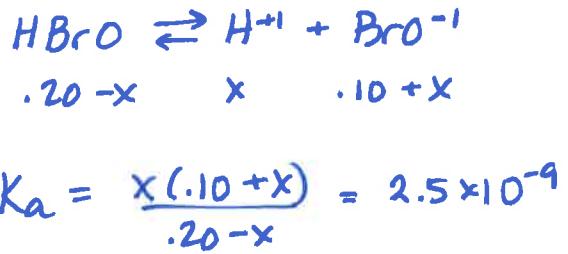
$\dfrac{x(.10)}{(.20)} = 2.5\times10^{-9}$

$x = [H^+] = 5.0\times10^{-9}$

$\boxed{pH = 8.30}$

← these could be done as Ka or Kb since acid and base are present

---

k. 0.040 M $C_6H_5NH_2$ weak base, $K_b = 4.3\times10^{-10}$

$C_6H_5NH_2 + H_2O \rightleftharpoons OH^{-1} + C_6H_5NH_3^{+1}$

$.040 - x \qquad\qquad x \qquad x$

$K_b = \dfrac{x^2}{.040 - x} = 4.3\times10^{-10}$

ass. $x \ll .040$

$\dfrac{x^2}{.040} = 4.3\times10^{-10}$

$x = [OH^-] = 4.1(5)\times10^{-6} M$

$pH = \boxed{8.62}$

---

l. 0.040 M $C_6H_5NH_3Br$

$C_6H_5NH_3^{+1} / Br^{-1}$

weak acid

$Ka = \dfrac{Kw}{Kb(C_6H_5NH_2)} = \dfrac{10^{-14}}{4.3\times10^{-10}} = 2.3(26)\times10^{-5}$

$C_6H_5NH_3^{+1} \rightleftharpoons C_6H_5NH_2 + H^{+1}$

$0.40 - x \qquad\qquad x \qquad x$

$Ka = \dfrac{x^2}{.040 - x} = 2.326\times10^{-5}$

ass. $x \ll .40$

$\dfrac{x^2}{.40} = 2.326\times10^{-5}$

$x = [H^+] = 0.0030(5) M$

$\boxed{pH = 2.52}$

---

m. A solution that is 0.040 M $C_6H_5NH_2$ and 0.050 M $C_6H_5NH_3Cl$

this could be done as a Kb or Ka since base and acid are present. I chose Kb.

$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^{+1} + OH^{-1}$

$.040 - x \qquad\qquad .050 + x \qquad x$

$K_b = \dfrac{x(.050 + x)}{(.040 - x)} = 4.3\times10^{-10}$

ass $x \ll .040, .050$
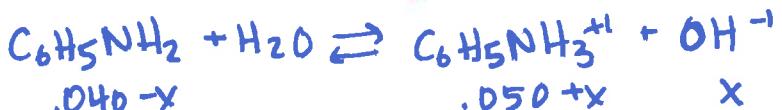
$\dfrac{x(.050)}{(.040)} = 4.3\times10^{-10}$

$x = [OH^-] = 3.4(4)\times10^{-10}$

$\boxed{pH = 4.54}$

**3.** For parts a-d: $\swarrow K_a = 2.5 \times 10^{-9}$

100. mL of 0.10 M HBrO are titrated with NaOH. 40.0 mL NaOH are required to reach the equivalence point.

a. Find the molarity of the NaOH.
b. Find the pH during the titration after 0, 20, 30, and 40 mL of NaOH have been added.
c. For which of the above volumes does a buffer solution exist in the flask?
d. Sketch the titration curve.

a)  @ EQ pt, moles HBrO = moles NaOH

$$M_a V_a = M_b V_b$$

$$(.10M)(100.mL) = M_b(40.0 \, mL) \qquad \boxed{M_b = 0.25 \, M}$$

---

ⓑ  **0 mL NaOH added**

here we just have weak
acid (HBrO) so do $K_a$.
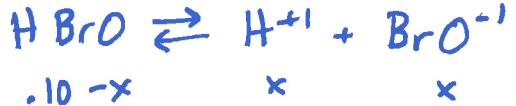
$$HBrO \rightleftharpoons H^{+1} + BrO^{-1}$$
$$.10-x \qquad x \qquad x$$

$$K_a = \frac{x^2}{.10-x} = 2.5 \times 10^{-9} \qquad \frac{x^2}{.10} = 2.5 \times 10^{-9}$$

ass. $x \ll .10$

$$x = [H^+] = 1.58 \times 10^{-5} M$$

$$\boxed{pH = 4.80}$$

**20 mL NaOH added**

here we are halfway to the equivalence point;
half the HBrO ~~to~~ has been converted to $BrO^{-1}$

$[HBrO] = [BrO^{-1}]$   so $pH = pK_a = -\log(2.5 \times 10^{-9}) = \boxed{8.60}$
(or do the 20 mL problem using same method as we used @ 30 mL)
                                                                    (below)

---

**30 mL NaOH added**

first react the strong base (free OH-) until something runs
out.

$$OH^{-1} + HBrO \rightarrow BrO^{-1} + H_2O$$

.0075 moles  .010 moles       0
$-.0075$      $-.0075$        $+.0075$
_____   _____    _____
  0          .0025 moles     .0075 moles

$$[HBrO] = \frac{.0025 \, moles}{0.130 \, L} = .01923 \, M$$

$$[BrO^{-1}] = \frac{.0075 \, mole}{.130 \, L} = .05769 \, M$$

now do $K_a$ (or $K_b$)

$$HBrO \rightleftharpoons H^{+1} + BrO^{-1}$$
$$.01923-x \qquad x \qquad .05769+x$$

$$K_a = \frac{x(.05769+x)}{.01923-x} = 2.5 \times 10^{-9}$$

ass. $x \ll .019, .058$

$$\frac{x(.05769)}{.01923} = 2.5 \times 10^{-9}$$

(tho we actually
lose a sig fig
in subtract
so just
1sf, 1 dec.
place
pH 9.1

$$x = [H^+] = 8.3 \times 10^{-10}$$

$$\boxed{pH = 9.08}$$

**3.** 100. mL of 0.10 M HBrO are titrated with NaOH. 40.0 mL NaOH are required to reach the equivalence point.
  a. Find the molarity of the NaOH.
  b. Find the pH during the titration, after 0, 20, 30, and 40 mL of NaOH have been added.
  c. For Which of the above volumes does a buffer solution exist in the flask?
  d. Sketch the titration curve.

③b cont'd    pH @ 40 mL NaOH   (@ EQ. Pt)

$$OH^- + HBrO \rightarrow BrO^{-1} + H_2O$$

| 0.010 | .010 moles | 0 |
| -.010 | -.010 | +.010 |
| 0 | 0 | 0.010 |

$$[BrO^-] = \frac{.010 \text{ mole}}{.140 L} = 0.071429 \text{ M } BrO^{-1} \quad (a \text{ weak base})$$

__K_b__

$$BrO^{-1} + H_2O \rightarrow OH^- + HBrO$$

.071429 -x              x        x

$$K_b(BrO^-) = \frac{K_w}{K_a(HBrO)}$$

$$K_b = \frac{10^{-14}}{2.5 \times 10^{-9}} = 4.0 \times 10^{-6}$$

$$K_b = \frac{x^2}{.071429 - x} = 4.0 \times 10^{-6}$$

ass. $x \ll .071429$

$$\frac{x^2}{.071429} = 4.0 \times 10^{-6}$$

$$x = [OH^-] = 0.00053 \text{ M}$$

$$\boxed{pH = 10.73}$$
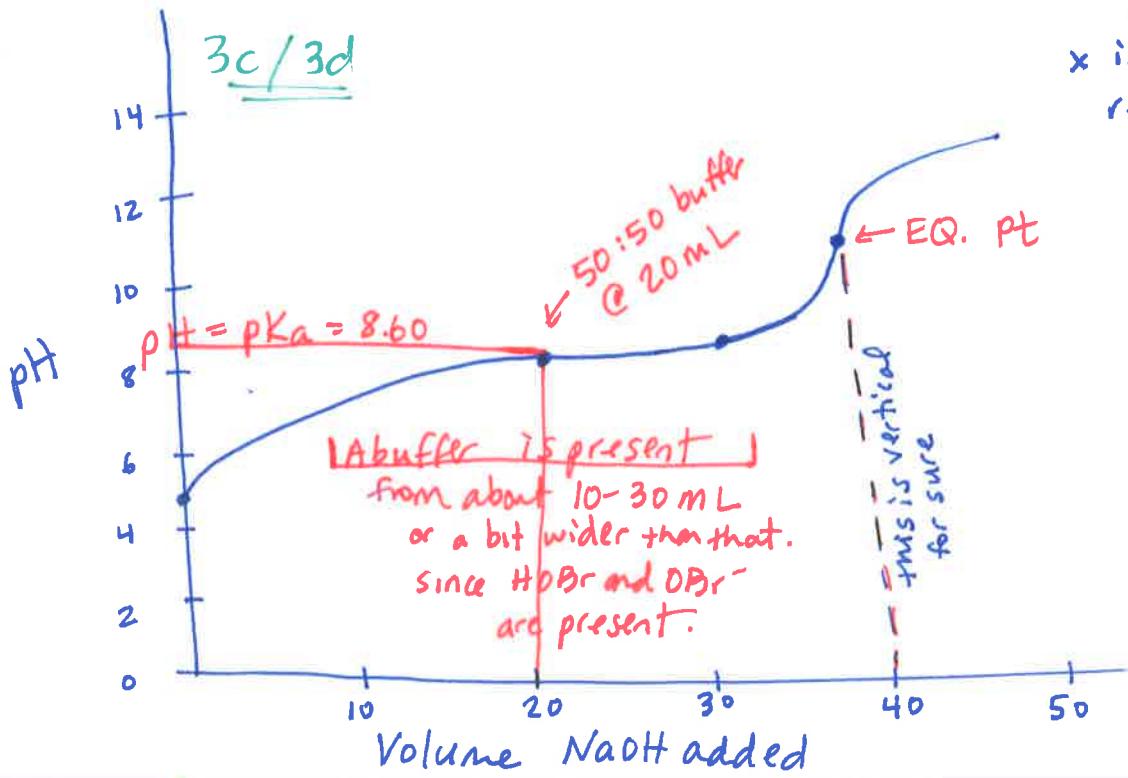
x is a bit large -
really should
have replugged in
or done Quadratic ...

**3c / 3d**



pH = pKa = 8.60

50:50 buffer
@ 20 mL

← EQ. Pt

A buffer is present
from about 10-30 mL
or a bit wider than that.
since HOBr and OBr⁻
are present.

this is vertical for sure

Volume NaOH added

**3.** For parts e-g:

50. mL of 1.2 M $(CH_3)_3N$ are titrated with 0.75 M $HNO_3$.

e. What volume of $HNO_3$ will be needed to reach the equivalence point?

f. Calculate the pH during the titration after 0, 15, 40, 65, 80, and 85 mL have been added.

g. For which of the above volumes does a buffer solution exist in the flask?

h. Sketch the titration curve.

e) $M_a V_a = M_b V_b$

$(0.75 M)(V_a) = (1.2 M)(50. mL)$

$$\boxed{V_a = 80. \, mL}$$

(f) @ 0 mL, we have 1.2 M $(CH_3)_3N$, a weak base, so do $K_b$.

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

1.2 -X          X          X
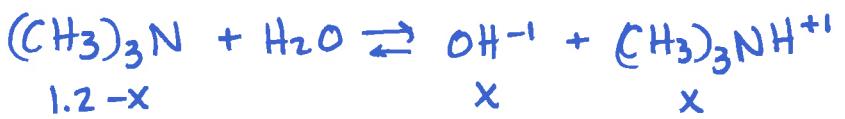
$K_b = \dfrac{X^2}{1.2-X} = 6.4 \times 10^{-5}$    ass. $X \ll 1.2$    $\dfrac{X^2}{1.2} = 6.4 \times 10^{-5}$

$X = [OH^-] = 0.00876 \, M$

$$\boxed{pH = 11.94}$$ @ 0 mL

(f) @ 15 mL:

first neutralize the added $H^{+1}$ ($HNO_3$)
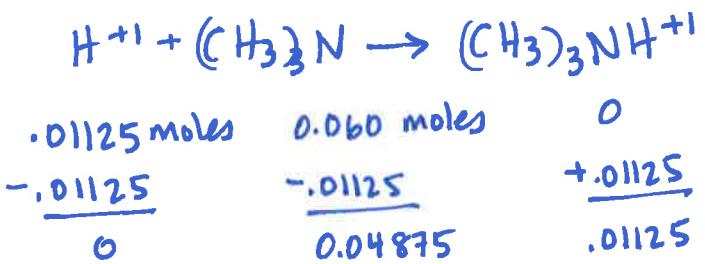
$H^{+1} + (CH_3)_3N \longrightarrow (CH_3)_3NH^{+1}$

$(.015 L)(.75 M) = .01125$ moles $H^{+1}$

$(.050 L)(1.2 M) = .060$ moles $(CH_3)_3N$

.01125 moles    0.060 moles        0

−.01125          −.01125          +.01125

0              0.04875          .01125

$[(CH_3)_3N] = \dfrac{.04875}{.065 L} = 0.75 \, M$    $[(CH_3)_3NH^{+1}] = \dfrac{.01125}{.065 L} = 0.173 \, M$

Then do $K_b$ (or $K_a$)

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

.75 -X                      .173 +X      X
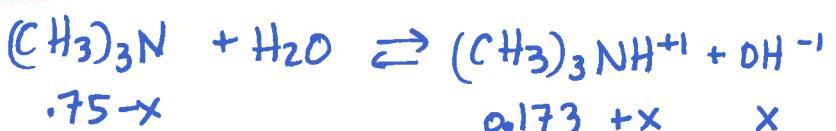
$\dfrac{X(.173)}{(.75)} = 6.4 \times 10^{-5}$

$X = [OH^-] = 0.000277 \, M$

$K_b = \dfrac{X(.173+X)}{(.75-X)} = 6.4 \times 10^{-5}$    ass. $X \ll .75$

$$\boxed{pH = 10.44}$$ @ 15 mL

**#3** (f) cont'd : 40 mL HNO3 added.

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

| .030 | .060 | 0 | |
|------|------|-----|---|
| -.030 | -.030 | +.030 | ) these are moles |
| 0 | .030 | .030 | |

So $[(CH_3)_3N] = [(CH_3)_3NH^{+1}] = \dfrac{.030 \text{ mole}}{.090L} = 0.33$ M

At this point you could do a $K_a$ or $K_b$ w/ the .33 M

or you could say (since we're halfway to the EP)

$$pH = pKa = -\log (K_a \text{ of } (CH_3)_3NH^{+1})$$

$$= -\log \left( \frac{K_w}{K_b (CH_3)_3N} \right) =$$

$$= -\log \left( \frac{10^{-14}}{6.4 \times 10^{-5}} \right)$$

$$= -\log (1.5625 \times 10^{-10})$$

$$\boxed{pH = 9.81}$$

or, $pOH = pK_b = -\log (6.4 \times 10^{-5}) = 4.19$

$$pH = 14 - pOH = \boxed{9.81} \quad @ 40 \text{ mL}$$

#3 (f) Cont'd          pH @ 65 mL $HNO_3$ added

$(.065 L)(.75 \frac{mole}{L}) = 0.04875$ moles $H^{+1}$ ($HNO_3$)

$(.050 L)(1.2 \frac{mol}{L}) = .060$ moles $(CH_3)_3N$

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

| | | |
|---|---|---|
| .060 | .04875 | 0 |
| -.04875 | -.04875 | +.04875 |
| .01125 | 0 | .04875 |
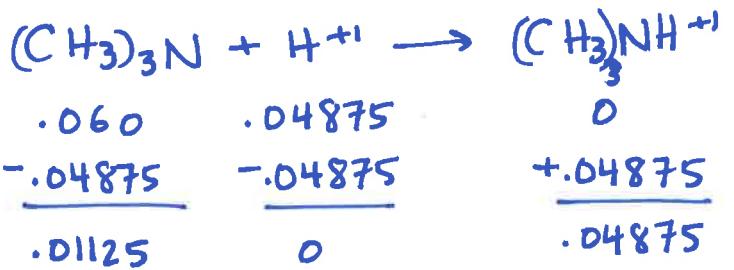
first Neutralize the
    $H^{+1}$ ion
these are in moles —
could do in molarity too

so $(CH_3)_3N = \frac{.01125 \, mole}{0.115 L} = 0.09783 \, M$

$(CH_3)_3NH^{+1} = \frac{.04875 \, mole}{0.115 L} = 0.42391 \, M$

now do a $K_b$ (or $K_a$) calc.

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

.09783-x                      .42391+x        x

$K_b = \frac{x(.42391+x)}{(.09783-x)} = 6.4 \times 10^{-5}$

ass. $x \ll .0978$ and $.4239 \, M$

$\frac{x(.42391)}{(.09783)} = 6.4 \times 10^{-5}$

$x = [OH^-] = 1.4(77) \times 10^{-5} \, M$

$pH = 14 + \log(1.477 \times 10^{-5}) = \boxed{9.17}$ @ 65 mL

#3 (f) contd    pH @ 80 mL $HNO_3$ added (EQ pt!)

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

| .060 mole | .060 mole | 0 |
| -.060 | -.060 | +.060 |
| 0 | 0 | .060 |

$[(CH_3)_3NH^+] = \dfrac{.060 \text{ mole}}{0.130 L} = 0.4615$ M

no base is left.. only weak acid present in flask, so do $\underline{\underline{Ka}}$

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

0.4615 M − x      x      x

$Ka = \dfrac{x^2}{.4615 - x} = 1.56 \times 10^{-10}$

$Ka \,(CH_3)_3NH^{+1} = \dfrac{Kw}{Kb\,(CH_3)_3N}$

$Ka = \dfrac{10^{-14}}{6.4 \times 10^{-5}} = 1.56 \times 10^{-10}$

ASS.  $x \ll .4615$

$\dfrac{x^2}{.4615} = 1.56 \times 10^{-10}$

$x = [H^+] = 8.49 \times 10^{-6}$ M

$\boxed{pH = 5.07}$ @ 80 mL EQ pt

---

pH @ 85 mL  (past the EP)

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

| .06375 | .060 mole | 0 |
| -.060 | -.060 | +.060 |
| .00375 | 0 | .060 |

(g and h on next page)

↑
strong acid
use this to
find pH.

↑
weak acid
(ignore, since
a strong acid
is also present)

$[H^+] = \dfrac{.00375 \text{ mole}}{0.135 L} = 0.0277 M$  ← actually 1 SF since we lost one in subtraction

$pH = -\log(.0277) = 1.56 \rightarrow \boxed{1.6}$ ← so just 1 dec. plac.

# 3 (g) and (h)

h) graph:
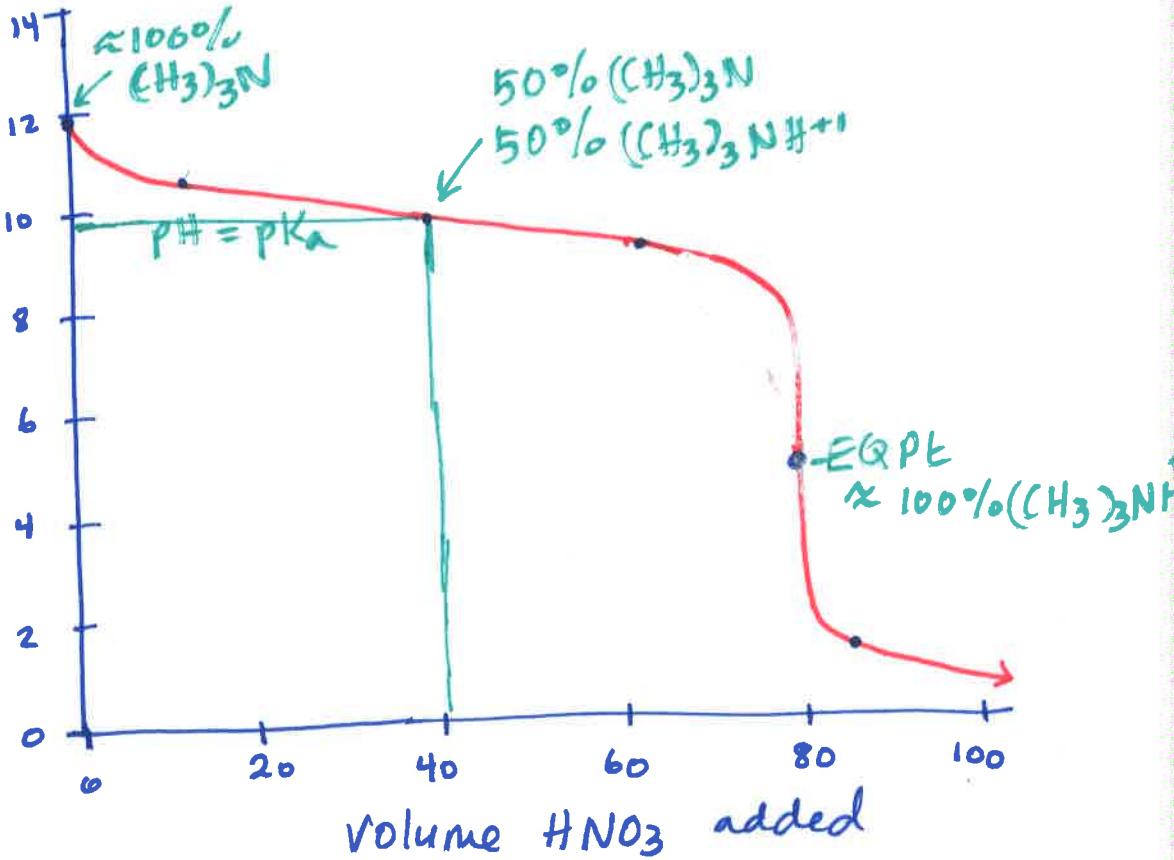


It is a buffer solution from $\approx 10$ mL to $\approx 70$ mL

or $\approx 15$ to $65$ mL

So it is a buffer @ {$15$ mL, $40$ mL, and $65$ mL} } weak ⌄ since acid and conj. base present

but **not** at $0$ mL (only weak base present)

and **not** at $80$ or $85$ mL (only acid present)

It works unless the anion is the (conj.) base of a strong acid.

**4a.** Which of these "insoluble" compounds will be more soluble when acid is added?

(BaCO₃)    ~~PbCl₂~~    (Cu(OH)₂)    (MgO)    ~~AgI~~    (MgF₂)

**4b.** For compounds you chose in (a), write a net ionic rxn showing the solid compound dissolving into strong acid. (Balance and do phase subscripts).

**4c.** If you want to have a silver ion concentration of 0.10 M, and a carbonic acid concentration of 0.080 M, what pH range is needed to avoid precipitation of silver carbonate?

**4d.** CuF is more soluble at low pH than at high pH. Explain why.
Include a discussion of the ratio of [F-] to [HF] as part of your answer.

**4b**

$$BaCO_{3(s)} + H^{+1}_{(aq)} \rightarrow Ba^{+2}_{(aq)} + HCO_3^{-1}_{(aq)}$$

OR

$$BaCO_{3(s)} + 2H^{+1}_{(aq)} \rightarrow Ba^{+2}_{(aq)} + H_2CO_{3(aq)}$$

↑
could split up
or not into $H_2O + CO_2$

$$Cu(OH)_{2(s)} + 2H^{+1}_{(aq)} \rightarrow Cu^{+2}_{(aq)} + 2H_2O_{(\ell)}$$

$$MgO_{(s)} + 2H^{+1}_{(aq)} \rightarrow Mg^{+2}_{(aq)} + H_2O_{(\ell)}$$

$$MgF_{2(s)} + 2H^{+1}_{(aq)} \rightarrow Mg^{+2}_{(aq)} + 2HF_{(aq)}$$

↑
HF is a **weak** acid so
it (mostly) stays together;
it doesn't split into ions.

If you tried rxns for PbCl₂ or AgI, it doesn't work:

$$PbCl_{2(s)} + 2H^{+1}_{(aq)} \rightarrow Pb^{+2}_{(aq)} ~~+ 2HCl_{(aq)}~~ \quad NR$$

$$AgI_{(s)} + H^{+1}_{(aq)} \rightarrow Ag^{+1}_{(aq)} ~~+ HI_{(aq)}~~ \quad NR$$

HCl and HI are **strong** acids so
they'll just split into H⁺ and Cl⁻/I⁻
so they won't reduce the amount
of Cl⁻ or I⁻ in solution.

**4a.** Which of these "insoluble" compounds will be more soluble when acid is added?

$BaCO_3$    $PbCl_2$    $Cu(OH)_2$    $MgO$    $AgI$    $MgF_2$

**4b.** For compounds you chose in (a), write a net ionic rxn showing the solid compound dissolving into strong acid. (Balance and do phase subscripts).

**4c.** If you want to have a silver ion concentration of 0.10 M, and a carbonic acid concentration of 0.080 M, what pH range is needed to avoid precipitation of silver carbonate?

**4d.** CuF is more soluble at low pH than at high pH. Explain why. Include a discussion of the ratio of [F-] to [HF] as part of your answer.

(c) $Ag_2CO_{3\,(s)} \rightleftharpoons 2\,Ag^{+1}_{(aq)} + CO_3^{-2}_{(aq)}$
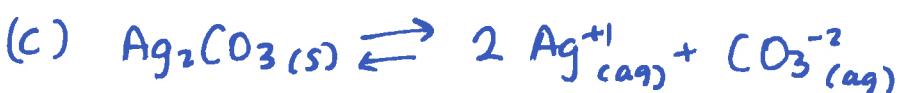
$K_{sp} = [Ag^{+1}]^2 [CO_3^{-2}] = 8.1 \times 10^{-12}$

$(.10)^2 [CO_3^{-2}] = 8.1 \times 10^{-12}$

$[CO_3^{-2}]_{max} = 8.1 \times 10^{-10} \, M$

$$\frac{[H^+]^2 (8.1 \times 10^{-10})}{(.080)} = 2.408 \times 10^{-7}$$

$[H^+]_{min} = 4.88 \times 10^{-5} \, M$

$H_2CO_3 \rightleftharpoons H^{+1} + HCO_3^{-1}$

$HCO_3^{-1} \rightleftharpoons H^{+1} + CO_3^{-2}$

$H_2CO_3 \rightleftharpoons 2\,H^{+1} + CO_3^{-2}$

$K_{eq} = K_{a1} \cdot K_{a2} = \dfrac{[H^+]^2 [CO_3^{-2}]}{[H_2CO_3]}$

$K_{eq} = (4.3 \times 10^{-7})(5.6 \times 10^{-11})$

$K_{eq} = 2.408 \times 10^{-17}$

$\boxed{pH = 4.31 \text{ or below}}$

(d) The [F-] must stay low to avoid precipitation of $CuF_{(s)}$

$Q_{sp} = [Cu^{+1}][F^-]$

if [F-] stays small, then $Q_{sp}$ will be small..

$Q_{sp}$ must be less than (or equal to) $K_{sp}$ to avoid precipitation.

$HF \rightleftharpoons H^{+1} + F^{-1}$

$K_a = \dfrac{[H^+][F^-]}{[HF]}$

$[F^-] = \dfrac{K_a}{[HF]} \quad [H^+]$

→ the lower the pH, the greater the [H+], and the lower the ratio of [F-] to [HF] (lots of $H^{+1}$ available, so the rxn $(HF \rightleftharpoons H^{+1} + F^{-1})$ shifts left.)

So adding $H^{+1}$ (lowering the pH) will increase [HF] and reduce [F-], so $Q_{sp}$ can stay low.

$K_{a_1} = 4.3 \times 10^{-7}$   $K_{a_2} = 5.6 \times 10^{-11}$

**5.** Find the pH, % ionization, $[H^{+1}]$, $[H_2CO_3]$, $[HCO_3^{-1}]$, and $[CO_3^{-2}]$ in a 0.10 M solution of carbonic acid.

$H_2CO_{3(aq)} \rightleftharpoons H^{+1} + HCO_{3(aq)}^{-1}$

.10 M $-x$          $x$          $x$
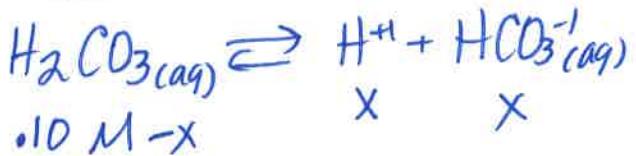
$K_{a_1} = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$

$\dfrac{x^2}{.10 - x} = 4.3 \times 10^{-7}$

assume $x \ll .10$

$\dfrac{x^2}{.10} = 4.3 \times 10^{-7}$

$x = .0002074$ M

$x = [H^+] = [HCO_3^-] = .00021$ M

$pH = -\log(.0002074) = 3.68$

$\dfrac{.0002074}{.10} \times 100 = 0.21 \%$ ionization

$HCO_3^{-1} \rightleftharpoons H^{+1} + CO_3^{-2}$
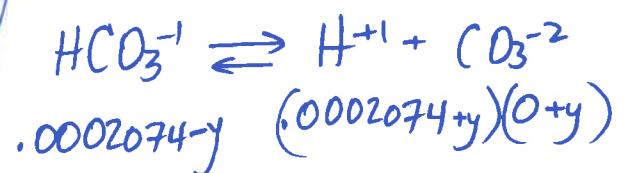
.0002074 $-y$   (.0002074 $+y$)(0 $+y$)

$K_{a_2} = \dfrac{(.0002074 + y)(y)}{(.0002074 - y)} = 5.6 \times 10^{-11}$

assume $x \ll .0002074$     $y = 5.6 \times 10^{-11}$

$[CO_3^{-2}] = 5.6 \times 10^{-11}$ M

**6.** Identify each compound as acidic, basic, or neutral, when it is dissolved in water.

KOH $K^{+1}/OH^{-1}$ **BASE**

HBr $H^{+1}/Br^{-1}$ **ACID**

NaH $Na^{+1}/H^{-1}$ **BASE**
neutral basic $H^{-1} + H_2O \rightarrow OH^- + H_{2(g)}$

Na$_2$HPO$_4$ **BASE** since $K_b > K_a$
$K_a(HPO_4^{-2}) = K_{a3}$ of $H_3PO_4 = 4.2\times10^{-13}$
$K_b(HPO_4^{-2}) = K_w/K_{a2}(H_3PO_4) = 1.6\times10^{-7}$

HCOOH
$H-\overset{\overset{\ddot{O}:}{\|}}{C}-\ddot{O}-H$ **ACID**

CH$_3$OH
$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\ddot{O}-H$ alcohol $\rightarrow$ **NEUTRAL**

CH$_3$CH$_2$NH$_2$
amine $\rightarrow$ **BASE**

CH$_3$CH$_2$NH$_3$Cl
$CH_3CH_2NH_3^{+1}/Cl^-$ **ACID**

SO$_3$ + H$_2$O $\rightarrow$ H$_2$SO$_4$
**ACID**

CaO
**BASE**

KClO$_2$
$K^{+1}/ClO_2^{-1}$ **BASE** since
$HClO_2$ = weak
neutral  so $ClO_2^{-1}$ = basic

NH$_4$I
$NH_4^{+1}/I^{-1}$
↑ neutral
↑
**ACID**

---

Ca(NO$_3$)$_2$ **NEUTRAL**   IA and IIA cations
are neutral
$NO_3^{-1}$ is c.b. of strong acid

C$_5$H$_5$NHI
$C_5H_5NH^{+1}$ **ACID**
and $I^{-1}$

HClO$_2$
**ACID**

LiNO$_2$
**BASE** ( $NO_2^{-1}$ is the c.b.
of a weak acid )

CH$_3$CH$_2$CH$_2$NH$_2$
**BASE** (amine)

CH$_3$CH$_2$CH$_2$OH
**NEUTRAL** (alcohol)

CH$_3$CH$_2$COOH
**ACID** $-\overset{}{C}-\overset{}{C}-\overset{\overset{:O:}{\|}}{C}-\ddot{O}-H$

CO$_2$ + H$_2$O $\rightarrow$ H$_2$CO$_3$
**ACID**

Na$_2$O
**BASIC** (oxide)

C$_5$H$_5$N
**BASE** (amine)

CH$_3$NH$_3$Br
$CH_3NH_3^{+1}/Br^{-1}$ **ACID**

KHSO$_3$
$K^{+1}/HSO_3^{-1}$
$K_a = 6.4\times10^{-8}$  **ACID**
$K_b = 6.7\times10^{-13}$  since $K_a > K_b$

**7.** The compound $C_{14}H_{14}N_3COOH$ has a pKa of 5.10.
This compound is an acid-base indicator. $C_{14}H_{14}N_3COOH$ is red, and $C_{14}H_{14}N_3COO^{-1}$ is yellow.

**a.** Calculate the Ka of $C_{14}H_{14}N_3COOH$.

$$K_a = 10^{-pK_a} = 10^{-5.10} = 7.943 \times 10^{-6} \rightarrow \boxed{K_a = 7.9 \times 10^{-6}}$$

**b.** Calculate the ratio of $[C_{14}H_{14}N_3COO^{-1}]$ to $[C_{14}H_{14}N_3COOH]$ when the pH is 4.10.

$$C_{14}H_{14}N_3COOH \rightleftarrows H^{+1} + C_{14}H_{14}N_3COO^{-1}$$
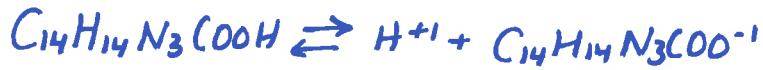
$$[H^+] = 10^{-4.10} = 7.943 \times 10^{-5} \, M$$

$$K_a = \frac{[H^+][C_{14}H_{14}N_3COO^-]}{[C_{14}H_{14}N_3COOH]}$$

$$\frac{[C_{14}H_{14}N_3COO^-]}{[C_{14}H_{14}N_3COOH]} = \frac{K_a}{[H^+]} = \frac{7.943 \times 10^{-6}}{7.943 \times 10^{-5}} = \boxed{0.10}$$

or $\frac{1}{10}$ ..
there is 10x more
[acid] than [conj. base]

**c.** Calculate the ratio of $[C_{14}H_{14}N_3COO^{-1}]$ to $[C_{14}H_{14}N_3COOH]$ when the pH is 5.10. ← pH = pKa

$$\frac{[C_{14}H_{14}N_3COO^-]}{[C_{14}H_{14}N_3COOH]} = \frac{K_a}{[H^+]} = \frac{7.943 \times 10^{-6}}{7.943 \times 10^{-6}} = \boxed{1.0}$$

so [acid] = [conj. base]
it is a 50/50 buffer!

**d.** Calculate the ratio of $[C_{14}H_{14}N_3COO^{-1}]$ to $[C_{14}H_{14}N_3COOH]$ when the pH is 6.10.

$$\frac{[conj.\ base]}{[acid]} = \frac{K_a}{[H^+]} = \frac{7.943 \times 10^{-6}}{7.943 \times 10^{-7}} = \boxed{10.}$$

So there is more
conjugate base than acid
(10 x more!)

**e.** In general, how does the ratio of $[C_{14}H_{14}N_3COO^{-1}]$ to $[C_{14}H_{14}N_3COOH]$ change as pH is raised? lowered?

The higher the pH, the higher the ratio of $\frac{[conj.base]}{[acid]}$

The lower the pH, the lower the ratio of [conjbase] / [acid]

So.. the more basic, the more conj. base is present! and vice versa.

**f.** At pH 4.1, 5.1, and 6.1, a solution containing this acid base indicator could be orange, yellow, or red.
   Which pH corresponds to which color?   mostly

Red at pH 4.1  Since the indicator is in acid ($C_{14}H_{14}N_3COOH$) form, which is red.

yellow at pH 6.1 since the indicator is most in base form, which is yellow.

orange at pH 5.1 { 50% = $C_{14}H_{14}N_3COOH$ = red
                  50% = $C_{14}H_{14}N_3COO^-$ = yellow }

**g.** What type of titration could this indicator be used for? (we want it to change color at the equivalence point)
   A weak acid being titrated with a strong base? Or a weak base being titrated with a strong acid?

[ pH = Basic @ EQ pt ]   [ pH = acidic at EQ Pt ]
                                    this one!

Since it changes color from pH 4-6 .. which is acidic.
(this is "methyl red" FYI)  It'll work for a titration with acidic EQ pt.

**8.** For each pair, circle the compound that would have the higher pH. Do this without a Ka/Kb chart.
(Assume each compound was dissolved at 0.10 M)

stronger acid → (HOCl)    or    (HOI)        Cl is more EN than I

basic    (NaClO$_2$)    or    (NaClO$_3$) neutral since HClO$_3$ is a strong acid

acid    AlCl$_3$    or    (NaCl) neutral

neutral   KCl    or    (KF) basic

acidic (ZnCl$_2$)    or    AlCl$_3$ ← more acidic since Al$^{+3}$ has higher charge than Zn$^{+2}$

acid    C$_2$H$_5$COOH    or    (C$_2$H$_5$CH$_2$OH) neutral

basic   (Ca(NO$_2$)$_2$)    or    Sn(NO$_3$)$_2$ acidic

acidic (Sn(NO$_3$)$_2$)    or    Sn(NO$_3$)$_4$ ← more acidic since Sn$^{+4}$ has higher charge than Sn$^{+2}$

**9. a.** Draw Lewis Dot Structures for HNO$_2$, HIO$_3$, and HIO.
**b.** Which is a stronger acid: HIO$_3$ or HIO? Why? Explain on a molecular level.
**c.** Which is a stronger acid: HIO$_3$ or HClO$_3$? Why? Explain on a molecular level.
**d.** Consider the compounds KIO, HBrO, HBrO$_2$, LiIO$_3$, NaClO$_3$, HBr.
Classify each one as acidic basic or neutral. If more than one compound is acidic/basic, which is the most acidic/basic (rank them all)?

**a)** HNO$_2$ 18 v.e.

H$-\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}$

HIO$_3$ 26 v.e.

H$-\ddot{\text{O}}-$I$-\ddot{\text{O}}$:
       |
     :O:

HIO 14 v.e.

H$-\ddot{\text{O}}-$I:

**c)** HClO$_3$ is stronger than HIO$_3$.
The HClO$_3$ structure is just like the HIO$_3$ structure, but with Cl replacing I.
Since Cl is more electronegative than I, the Cl pulls e$^-$ away from H more strongly than I can, increasing the polarity of the H-O Bond, and increasing the acid strength.
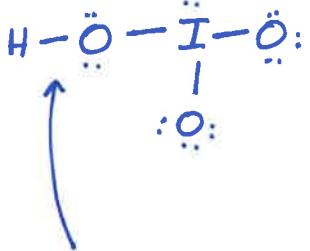
**b)** HIO$_3$ is a stronger acid than HIO. the additional oxygens attached to the I cause the H-O bond to be very polar, (more polar than the H-O bond in HIO) since the highly electronegative oxygen atoms pull e$^-$ through the molecule, away from H. The more polar the H-O bond, the more likely the H$^+$ is to "fall off," so the higher the % ionization and the stronger the acid.

KIO    HBrO    HBrO$_2$    LiIO$_3$   NaClO$_3$   HBr

base    acid    acid    base    ~~base~~ neutral   acid strongest acid (is a strong acid)
(most basic)  (3rd most acidic)  (2nd most acidic)

10. A Monoprotic acid is titrated with NaOH. Use the graph below to determine.
a. The molar mass of the acid.            b. The Ka of the acid.

## pH Titration Curve for 0.0500 M NaOH
### 0.2000 g of Unknown Acid "HX"



# 10

y-axis: pH
x-axis: Volume of NaOH Added
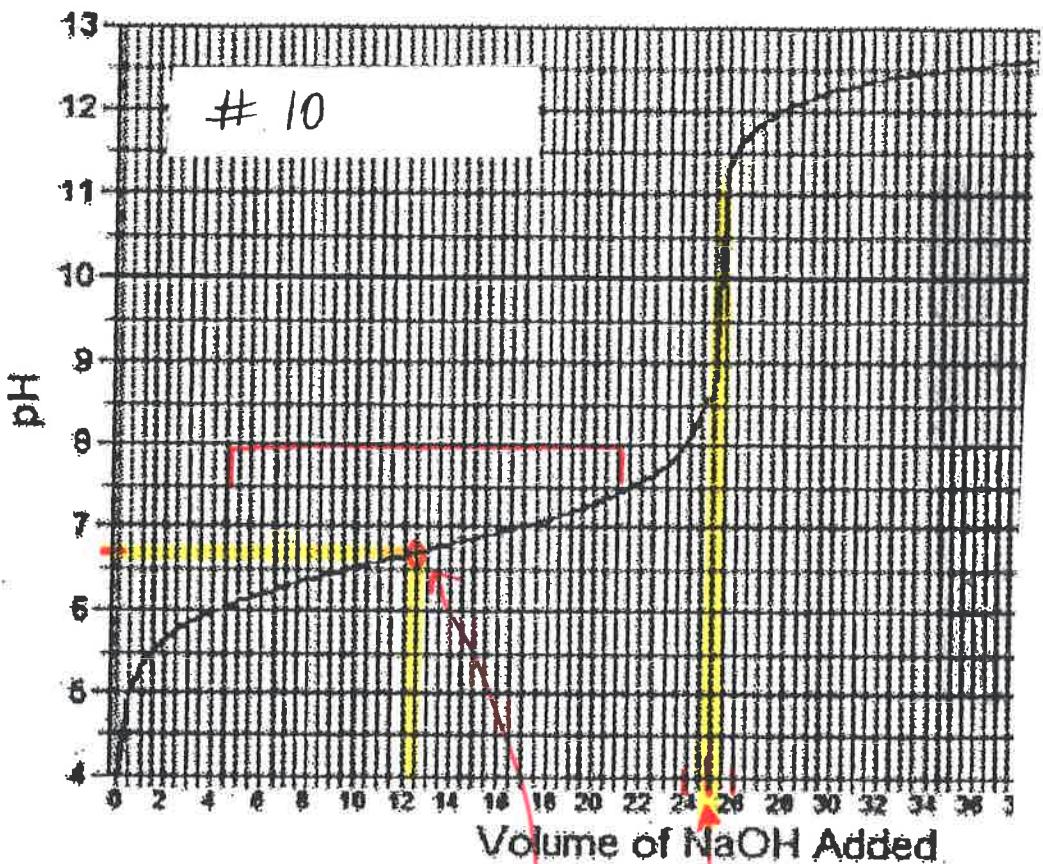
$\dfrac{25}{2} = 12.5\,mL$

$pKa = 6.7$

$Ka = 10^{-6.7} = $ ~~$200$~~

$\boxed{Ka = 2 \times 10^{-7}}$

50% HX
50% X⁻¹

EQ pt at 25 mL NaOH

at EQ pt, moles HX = mole NaOH

$(.025\ L\ NaOH)(.0500\ \tfrac{mole}{L}) = .00125$ moles NaOH or moles HX

$\dfrac{.2000\,g}{.00125\ moles} = \boxed{160\ \dfrac{g}{mole}}$

(if you use 25.5 mL at EQ pt you get 157 $\tfrac{g}{mole}$)

**11.** Calculate Keq for each reaction:

a.   $H^{+1} + OBr^{-1} \longleftrightarrow HOBr$   $\dfrac{\cancel{}}{K_a} + HOBr = \dfrac{1}{2.5 \times 10^{-9}} = \boxed{4.0 \times 10^8}$

b.   $OBr^{-1} + H_2O \longleftrightarrow HOBr + OH^{-1}$

$K_b \text{ of } OBr^{-1} = \dfrac{K_w}{K_a(HOBr)} = \dfrac{10^{-14}}{2.5 \times 10^{-9}} = \boxed{4.0 \times 10^{-6}}$

c.   $HOBr + OH^{-1} \longleftrightarrow OBr^{-1} + H_2O$

$\dfrac{1}{K_b(OBr^-)} = \dfrac{K_a(HOBr)}{K_w} = \dfrac{2.5 \times 10^{-9}}{10^{-14}} = \boxed{2.5 \times 10^5}$

d.   $2\,Ag^{+1}_{(aq)} + CO_3^{-2}{}_{(aq)} \longleftrightarrow Ag_2CO_{3(s)}$

$\dfrac{1}{K_{sp} \text{ of } Ag_2CO_3} = \dfrac{1}{8.1 \times 10^{-12}} = \boxed{1.2 \times 10^{11}}$

e.   $SO_3^{-2} + 2\,H^{+1} \longleftrightarrow H_2SO_3$

$\dfrac{1}{K_{a1} \cdot K_{a2}} = \dfrac{1}{(015)(6.4 \times 10^{-8})} = \boxed{1.0 \times 10^9}$

f.   $(CH_3)_3N + H_2O \longleftrightarrow (CH_3)_3NH^{+1} + OH^{-1}$

$K_b \text{ of } (CH_3)_3N = \boxed{6.4 \times 10^{-5}}$

g.   $H^{+1} + (CH_3)_3N \longleftrightarrow (CH_3)_3NH^+$

$\dfrac{1}{K_a\,(CH_3)_3NH^{+1}} = \dfrac{1}{\left(K_w / K_b(CH_3)_3N\right)} = \dfrac{K_b(CH_3)_3N}{K_w} = \dfrac{6.4 \times 10^{-5}}{10^{-14}}$

$= \boxed{6.4 \times 10^9}$
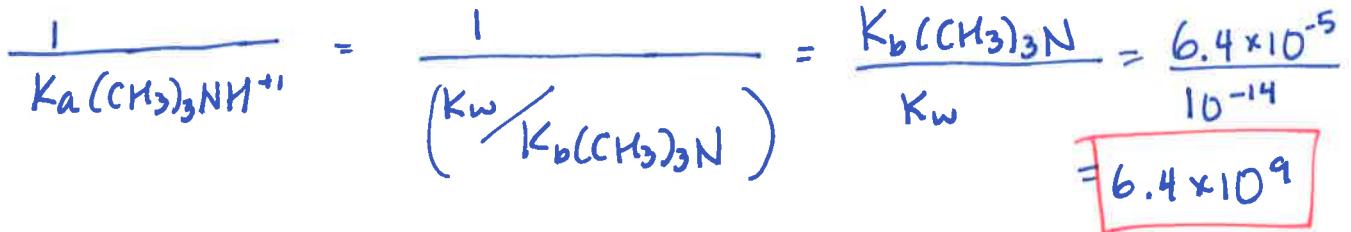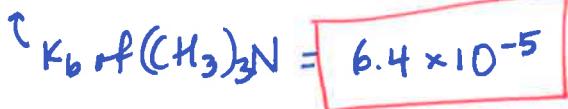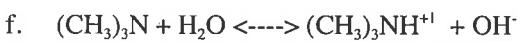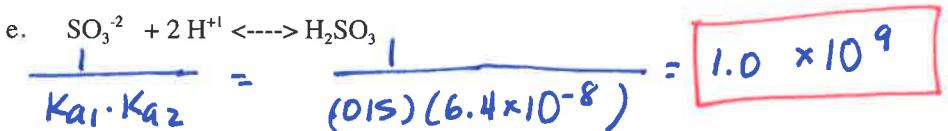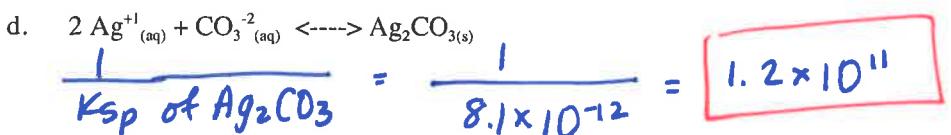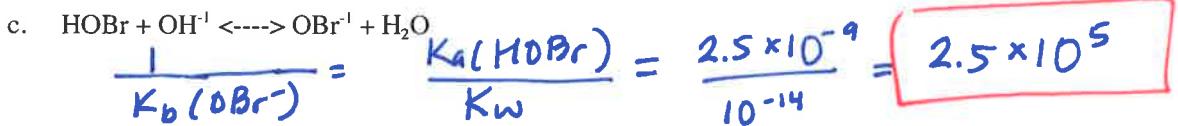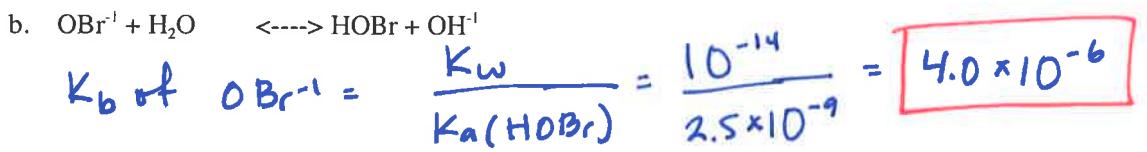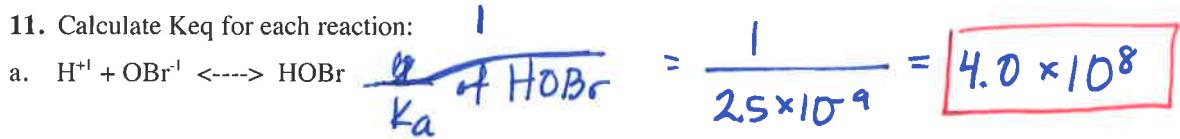
**12.** A titration curve for a diprotic acid is shown below. Label the graph:
Which ions/molecules ($H_2X$, $HX^{-1}$, or $X^{-2}$) are the main ones in the reaction flask at various places on the graph?
When is a buffer solution present, and what will be the approximate pH of the buffer solution?
Where are the equivalence points?



2nd EQ Pt
from here and beyond, →
nearly all is $X^{-2}$

buffer present

halfway between
$EP_1$ and $EP_2$

$[HX^{-1}] = [X^{-2}]$

← 1st EQ Pt
nearly all is $HX^{-1}$     $pH = pKa_2 \approx 9.5$

buffer present

nearly all is
$H_2X$

halfway to the first EQ Pt

$$[H_2X] = [HX^{-1}]$$

$$\text{and } pH = pKa_1 \approx 2.3 \text{ or } 2.4$$
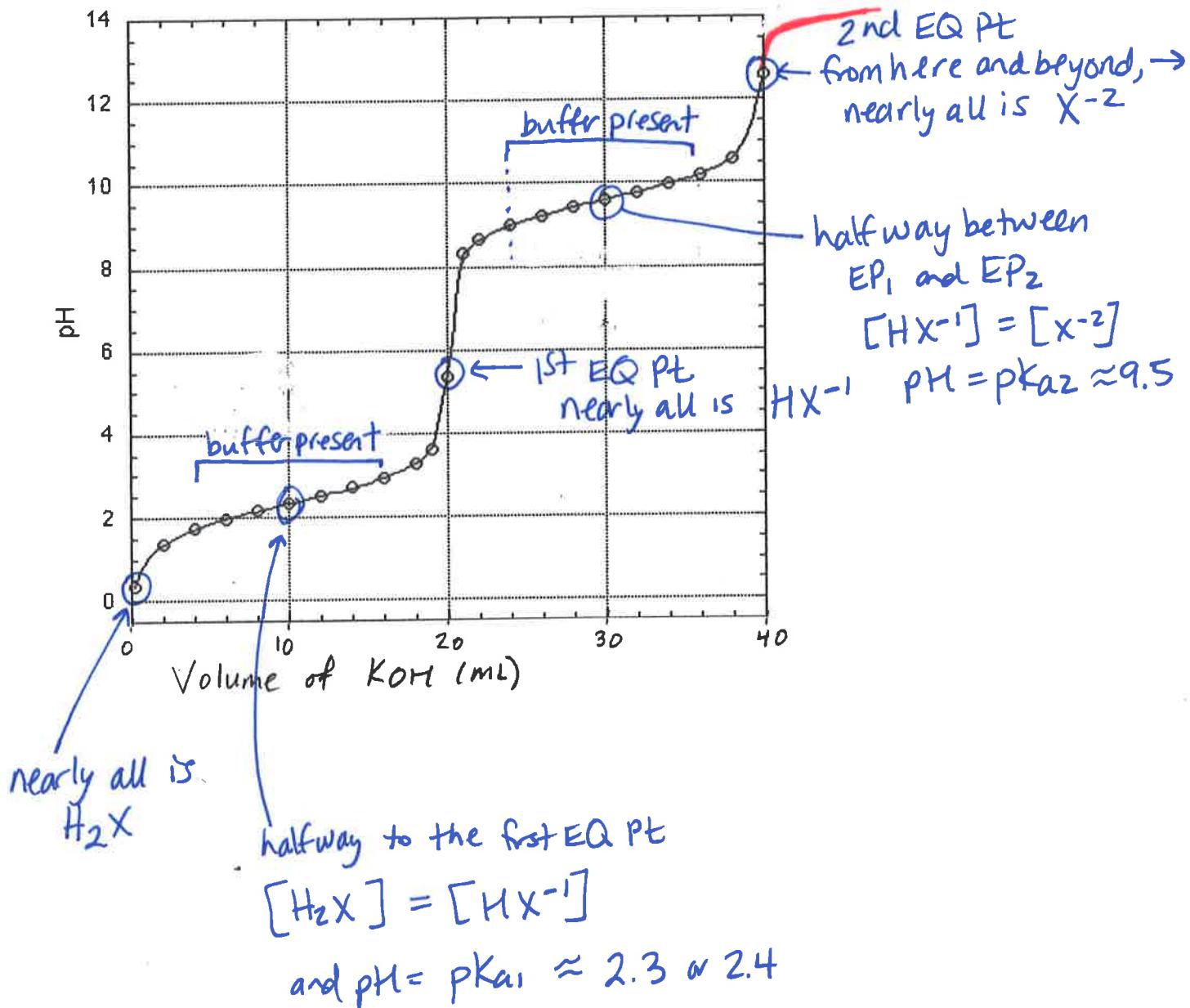
A buffer is present from $\approx 4\,mL$ to $\approx 16\,mL$
(or maybe 5 to 15 mL)
around pH of 2 to 3 (near the $pKa_1$)     } since $HX$ and $X^{-1}$ are present

A buffer is also present from $\approx 25\,mL$ to $35\,mL$
around pH of 9 to 10 (near the $pKa_2$)
Since $HX^{-1}$ and $X^{-2}$ are present.

$H_2CO_3/HCO_3^{-1}/CO_3^{-2}$

a. Which two compounds would you need to use to make a buffer with pH 10.00?
b. What should be the molarities of each compound in the buffer?
c. Which two compounds would you need to use to make a buffer with pH 6.10?
d. What should be the molarities of each compound in the buffer?

$H_2CO_3$: $K_{a_1} = 4.3 \times 10^{-7}$         $H_2CO_3 \rightleftarrows H^{+1} + HCO_3^{-1}$

$pK_{a_1} = 6.37$                  $K_{a_1} = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$

$K_{a_2} = 5.6 \times 10^{-11}$        $HCO_3^{-1} \rightleftarrows H^{+1} + CO_3^{-2}$
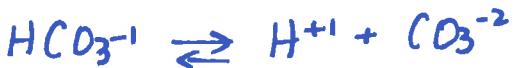
$pK_{a_2} = 10.25$            $K_{a_2} = \dfrac{[H^+][CO_3^{-2}]}{[HCO_3^{-1}]}$

a) to buffer @ pH 10.00, we need an __acid__
with a __pka of around 10.__
$HCO_3^{-1}$ has a $K_a$ of $5.6 \times 10^{-11}$ and pka of 10.25
so $HCO_3^{-1}$ must be our acid.
So $CO_3^{-2}$ will be our conj. base

So **$KHCO_3$ and $Na_2CO_3$ are needed**. (a)

$K_{a_2} = 5.6 \times 10^{-11} = \dfrac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = \dfrac{(10^{-10.00})[CO_3^{-2}]}{[HCO_3^-]}$

$\dfrac{[CO_3^{-2}]}{[HCO_3^-]} = \dfrac{5.6 \times 10^{-11}}{10^{-10}} = 0.56$

So use   **$[KHCO_3] = 1.0\ M$**   (b)   )   or other molarities
       **$[Na_2CO_3] = 0.56\ M$**           with the same ratio...

**b/** cont'd on nextpage!

(13) If you have these compounds available: $H_2CO_3$, $KHCO_3$, and $Na_2CO_3$

   a. Which two compounds would you need to use to make a buffer with pH 10.00?
   b. What should be the molarities of each compound in the buffer?
   c. Which two compounds would you need to use to make a buffer with pH 6.10?
   d. What should be the molarities of each compound in the buffer?

c) to make a buffer w/ pH 6.10,

we need an acid with a pka near 6.10

$H_2CO_3$ has a $Ka$ of $4.3 \times 10^{-7}$ and pKa of 6.37

so $H_2CO_3$ will be our acid.

HCO$_3^{-1}$ (conj. base of $H_2CO_3$) will be our base

So we'll use $H_2CO_3$ and $KHCO_3$.

$$Ka = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$4.3 \times 10^{-7} = \frac{10^{-6.10}[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 0.54$$

~~So use 0.54 M $H_2CO_3$~~

So use $\boxed{\begin{array}{l} [H_2CO_3] = 1.0 \text{ M} \\ [HCO_3^-] = 0.54 \text{ M} \end{array}}$ ) or different amounts, still with a 0.54 ratio.