

③ A buffer solution contains HX ($pK_a = 4.5$) and its conj. base (X^{-1}). If the soln pH is 4.3, predict how $[HX]$ compares to $[X^{-1}]$.
 If $pH = pK_a$, the concentrations of HX and X^{-1} would be equal.

The higher the ratio of $[HX]$ to $[X^{-1}]$, the more acidic the solution, and the lower the pH, and vice versa

if $[HX] > [X^{-1}]$ then $pH < pK_a$
 if $[X^{-1}] > [HX]$ then $pH > pK_a$

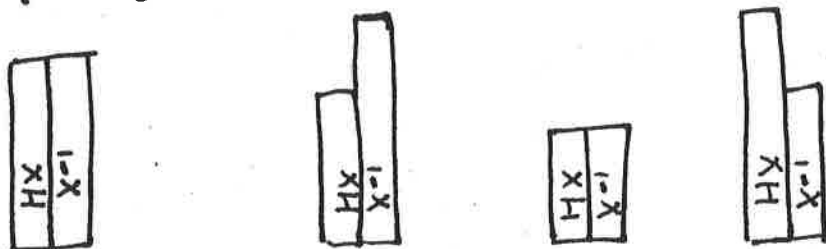
Since $pH (4.3) < pK_a (4.5)$,

$$\boxed{[HX] > [X^{-1}]}$$

(if we do a little math,

$$\frac{[H^+][X^{-1}]}{[HX]} = K_a \quad \frac{[X^{-1}]}{[HX]} = \frac{K_a}{[H^+]} = \frac{10^{-pK_a}}{10^{-pH}} = \frac{10^{-4.5}}{10^{-4.3}} = 10^{-0.2} < 1$$

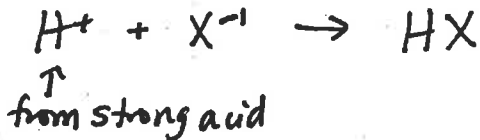
④



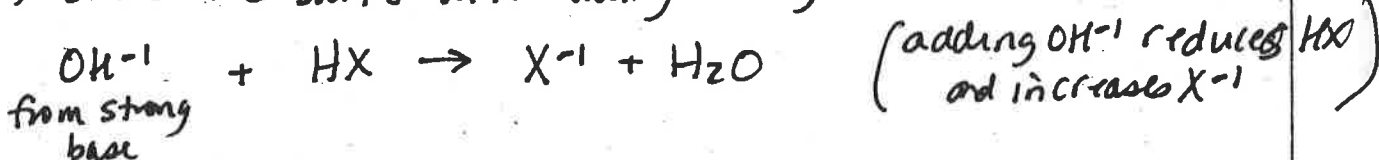
(original buffer

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

(a) (3) shows the original buffer after adding strong acid. adding H^{+1} reduces $[X^{-1}]$ and increases $[HX]$



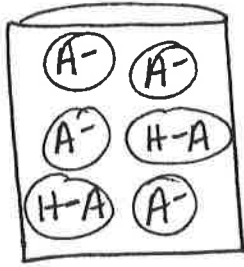
(b) (1) shows the buffer after adding strong base.



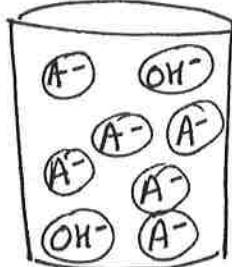
(c) (2) could not arise from adding strong acid or strong base since $[X^{-1}] = [HX]$ as in the original buffer.

as shown in (a) and (b), adding acid would increase HX while decreasing X^{-1} , and adding base would increase X^{-1} while decreasing HX. to arrive at situation (2), you could add H_2O to the original buffer, diluting the HX and X^{-1} concentrations.

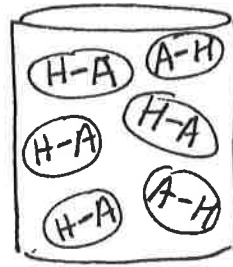
5.



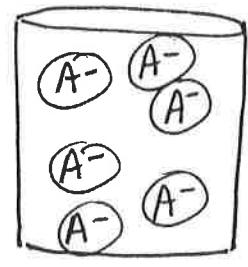
(i)



(ii)



(iii)



(iv)

(Na^+ and H_2O not shown)

A weak acid H-A is being titrated w/ NaOH .

(a) which beaker represents things before any base is added?

At this point, nearly all the acid is in the form of HA hardly any has ionized to release A^- since it is a weak acid. This is beaker (iii)

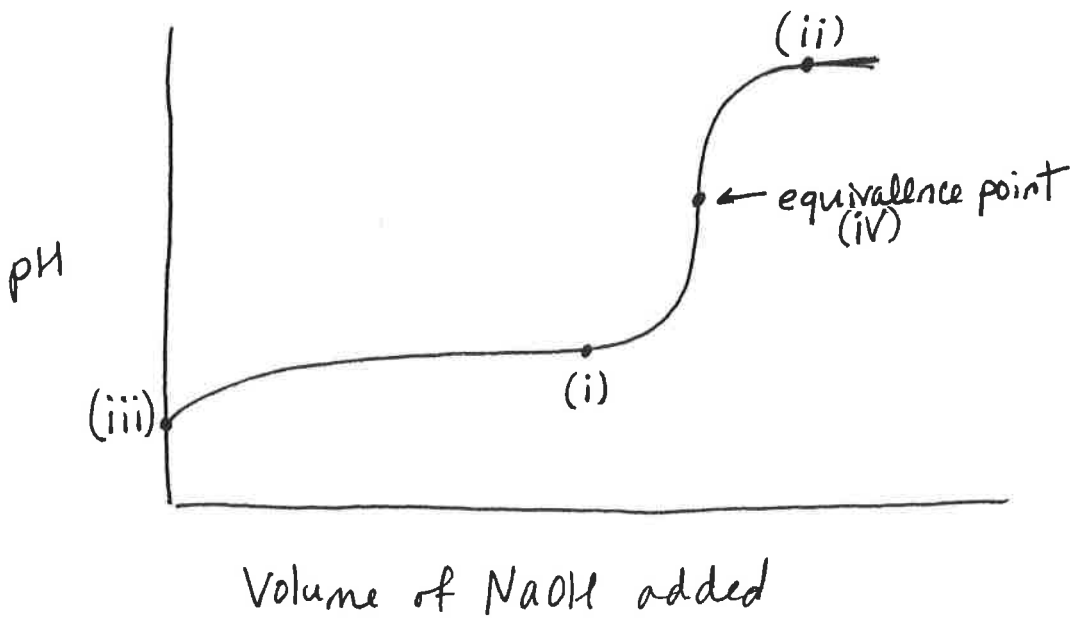
(b) which shows it after NaOH has been added, but before the equivalence pt?

At this point, some of the HA has been converted to A^- , and some HA remains. all the added OH^- has been used up so no OH^- is present. This is beaker (i)
 ↑
 or essentially no

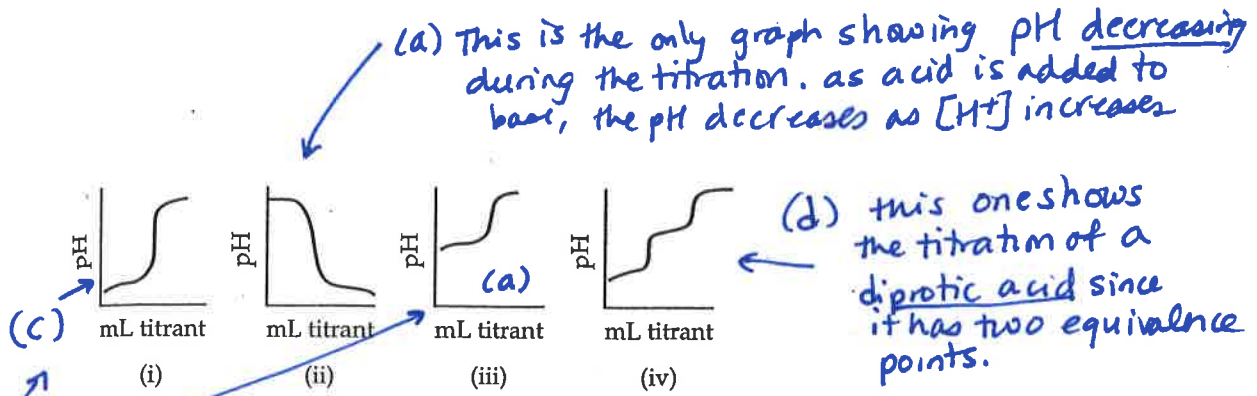
(c) At equivalence pt:

here, all the HA has been converted to A^- , but there is no excess OH^- . this is (iv)

(d) after the equivalence pt, all of the HA has been converted to A^- , plus there is an excess of OH^- . this is beaker (ii)

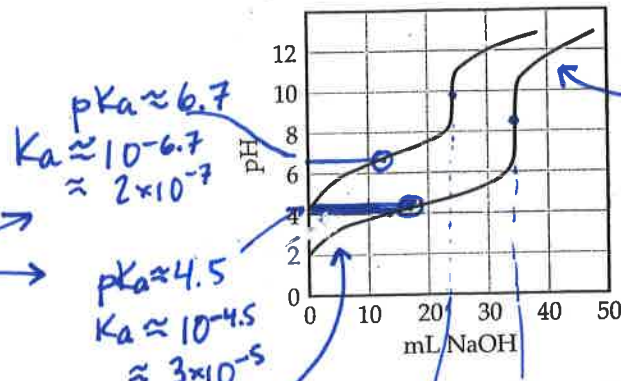


6. 17.6 Match the following descriptions of titration curves with the diagrams: (a) strong acid added to strong base, (b) strong base added to weak acid, (c) strong base added to strong acid, (d) strong base added to polyprotic acid. [Section 17.3]



Both of these show a monoprotic acid being titrated with a base.
 (a)/(ii) is the weak acid curve, since the initial pH and pH at the equivalence point are higher than they are on graph (i).
 a strong acid/strong base titration would be pH 7 at E.P.
 a weak acid/strong base titration would be pH > 7 (basic) at EP.

7. 17.7 Equal volumes of two acids are titrated with 0.10 M NaOH resulting in the two titration curves shown in the following figure. (a) Which curve corresponds to the more concentrated acid solution? (b) Which corresponds to the acid with the larger K_a ? Explain. [Section 17.3]

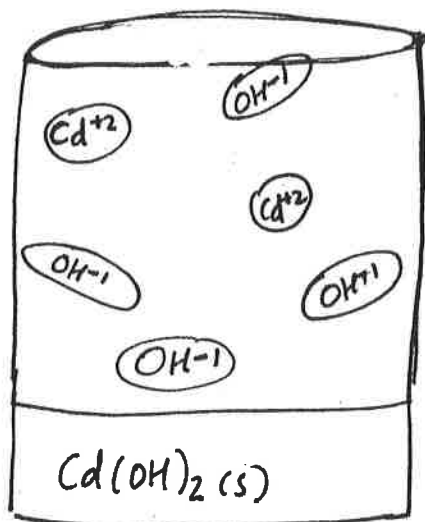


(a) this acid was more concentrated. It required a larger volume of NaOH (34 mL vs 24 mL) to reach the equivalence point.

(b) this acid also has the larger K_a value. It has a lower initial pH and lower pH at the equivalence pt.
 [you can estimate K_a from the graph by reading pH at halfway to equivalence point (at 12 mL and 17 mL).
 This acid has the higher K_a / lower pH / more acidic.

$V_b \approx 24 \text{ mL}$ $V_b \approx 34 \text{ mL}$ at Eq. pt

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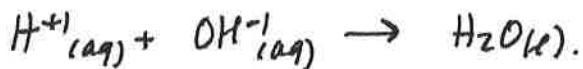
← Saturated solution of $\text{Cd}(\text{OH})_2$, with solid compound at bottom of beaker.

← 2:1 ratio of OH^- ions to Cd^{+2} ions

Adding acid will increase solubility of this compound, so more compound will dissolve. (Which beaker shows the new solution correctly?)

This works because H^+ ions (from added acid) can react with OH^- ions, decreasing the concentration of OH^- ions, temporarily decreasing Q_{sp} to below K_{sp} , until more solid dissolves, and Q_{sp} increases until $Q = K$.

The H^+ will react with the OH^- , but not with $\text{Cd}^{+2}(\text{aq})$



So $[\text{OH}^-]$ will decrease, but then more $\text{Cd}(\text{OH})_2(\text{s})$ will dissolve, creating $2\text{OH}^-(\text{aq})$ per every $1\text{Cd}^{+2}(\text{aq})$

The new solution will have less than a 2:1 ratio of OH^- to Cd^{+2} though, ~~so~~ since the acid reacted with OH^- only.

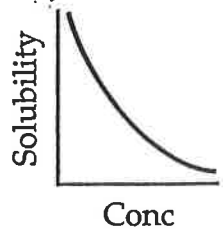
So the solution will look like Beaker A, since only A shows a $\text{OH}^-/\text{Cd}^{+2}$ ratio of less than 2:1

(A contained 8 Cd^{+2} , and 2 OH^- . B contained 4 Cd^{+2} and 8 OH^-)

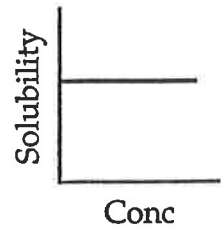
#9



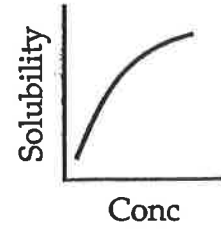
17.9 The following graphs represent the behavior of BaCO_3 under different circumstances. In each case the vertical axis indicates the solubility of the BaCO_3 and the horizontal axis represents the concentration of some other reagent. (a) Which graph represents what happens to the solubility of BaCO_3 as HNO_3 is added? (b) Which graph represents what happens to the BaCO_3 solubility as Na_2CO_3 is added? (c) Which represents what happens to the BaCO_3 solubility as NaNO_3 is added? [Section 17.5]



(b)

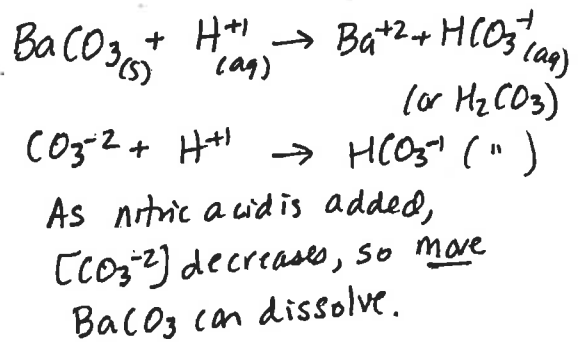


(c)



(a)

as Na_2CO_3 is added, $[\text{CO}_3^{-2}]$ will increase. The solubility equation will shift left; less $\text{BaCO}_3(s)$ will be able to dissolve.



Na^{+1} and NO_3^{-1} are not found in the solubility equation, so they will not affect the solubility of BaCO_3 .
 * and they don't affect the concentration of anything in the solubility equation.... something like NaNO_2 could affect things a bit, since NO_2^{-1} is weakly basic, and so could "steal" H^{+1} from HCO_3^{-1} , increasing $[\text{CO}_3^{-2}]$, and decreasing solubility of BaCO_3 .

- (20) Explain why mixing 100 mL of 0.100 M CH_3COOH with 50 mL of 0.100 M NaOH would create a buffer soln.

A buffer solution must contain a weak acid and its conjugate base (or vice versa), in fairly similar concentrations.

CH_3COOH is a weak acid. $(.100 \text{ L})(.100 \text{ M}) = .0100 \text{ moles } \text{CH}_3\text{COOH}$

$(.100 \text{ M})(.050 \text{ L}) = .0050 \text{ moles } \text{NaOH}$, a strong base

The OH^- from the NaOH can convert some of the acetic acid (CH_3COOH) into its conjugate base, acetate:

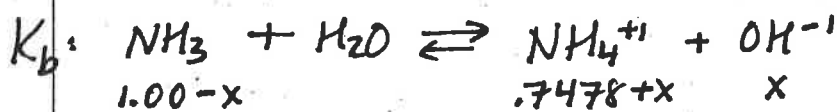


| | | | |
|---------|---------------|---------------|---------------|
| Initial | .0050 | .0100 | |
| Δ | <u>-.0050</u> | <u>-.0050</u> | <u>+.0050</u> |
| | 0 | .0050 moles | .0050 moles |

Once the OH^- reacts, we are left with equimolar amounts of CH_3COOH (a weak acid) and CH_3COO^- (the conj. base)

- (24) A buffer soln contains NH_4Cl and NH_3 :
10.0 g NH_4Cl were added to 250 mL of 1.00 M NH_3 .

(a) pH of solution: (I'm assuming no volume change when NH_4Cl was added) $\rightarrow .7478 \text{ M } \text{NH}_4^+$

$$\frac{(10.0 \text{ g } \text{NH}_4\text{Cl}) \left(\frac{1 \text{ mole}}{53.49139} \right)}{0.25 \text{ L}} = 0.7478 \text{ M } \text{NH}_4\text{Cl} \rightarrow .7478 \text{ M } \text{Cl}^-$$


$$K_b = \frac{(.7478 + x)(x)}{1.00 - x} = 1.8 \times 10^{-5}$$

assume $x \ll 1.00$, K_b of NH_3

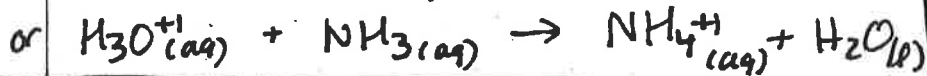
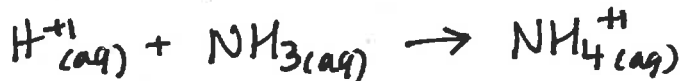
$$\frac{(.7478)(x)}{1.00} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = 2.4(07) \times 10^{-5}$$

$$\text{pOH} = 4.62$$

$$\text{pH} = 14 - \text{pOH} = \boxed{9.38}$$

- (b) if nitric acid is added to the buffer, the H^+ from the acid will react with the base in the buffer: NH_3



- (c) if KOH added to buffer, the OH^- from KOH will react with the acid in the buffer: NH_4^+



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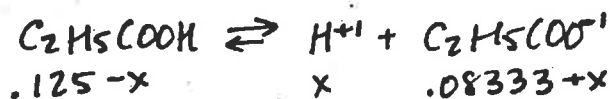
Buffer solution:

0.15 mole propionic acid, C_2H_5COOH (aka "propionic" acid)
 0.10 mole sodium propionate, C_2H_5COONa (aka sodium propionate)

(a) pH of buffer:

$$[C_2H_5COOH] = \frac{0.15 \text{ mole}}{1.20 \text{ L}} = 0.125 \text{ M}$$

$$[C_2H_5COO^-] = \frac{0.10 \text{ mole}}{1.20 \text{ L}} = 0.08333 \text{ M}$$



$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

$$\frac{x(.08333 + x)}{.125 - x} = 1.3 \times 10^{-5}$$

ass. $x \ll .125, .083$

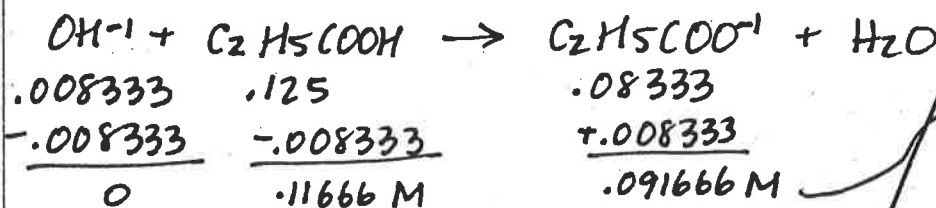
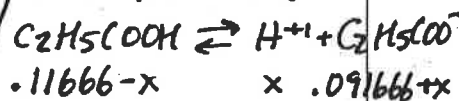
$$\frac{x(.08333)}{.125} = 1.3 \times 10^{-5}$$

$$x = [H^+] = 1.9(5) \times 10^{-5} \text{ M}$$

$$pH = -\log(1.95 \times 10^{-5}) = \boxed{4.71} \quad (a)$$

(b) if we add 0.01 moles NaOH to it:

assuming no ΔV → $[OH^-] = \frac{.01 \text{ mol}}{1.2 \text{ L}} = .008333 \text{ M OH}^-$
 before reacting w/ buffer.

OH⁻ will react with the acid in the buffer:Now do a K_a :

$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

$$\frac{(.091666 + x)x}{.11666 - x} = 1.3 \times 10^{-5}$$

ass. $x \ll .116, .0916$

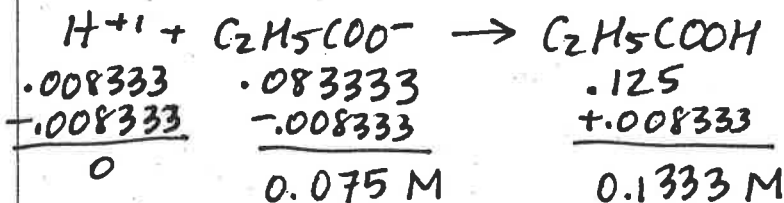
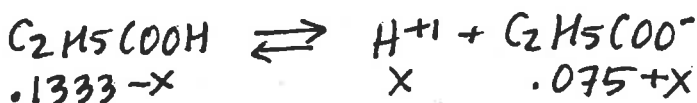
$$x = [H^+] = 1.6(5) \times 10^{-5}$$

$$pH = -\log[H^+] = \boxed{4.78} \quad (b)$$

(c) if we add .01 mole HI to it

$$[HI] = .01 \text{ mol} / 1.2 \text{ L} = .008333 \text{ mole/L}$$

before reacting.

the H⁺ will react w/ the base in the bufferNow, do a K_a !

$$K_a = \frac{x(.075 + x)}{.1333 - x} = 1.3 \times 10^{-5}$$

ass. $x \ll .133, .075$

$$x = [H^+] = 2.3 \times 10^{-5} \text{ M}$$

$$pH = -\log(2.3(1) \times 10^{-5}) = \boxed{4.64} \quad (c)$$

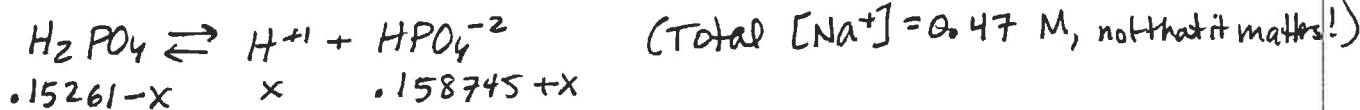
30

Buffer contains 6.5 g NaH_2PO_4 + 8.0 g Na_2HPO_4 in 355 mL

Find pH

$$\frac{(6.5 \text{ g NaH}_2\text{PO}_4) \left(\frac{1 \text{ mole}}{119.977 \text{ g}} \right)}{0.355 \text{ L}} = 0.15261 \text{ M} \rightarrow \begin{cases} [\text{Na}^+] = .15261 \text{ M} \\ [\text{H}_2\text{PO}_4^-] = .15261 \text{ M} \end{cases}$$

$$\frac{(8.0 \text{ g Na}_2\text{HPO}_4) \left(\frac{1 \text{ mole}}{141.9589 \text{ g}} \right)}{0.355 \text{ L}} = 0.158745 \text{ M} \rightarrow \begin{cases} [\text{Na}^+] = 0.31749 \text{ M} \\ [\text{HPO}_4^{2-}] = .158745 \end{cases}$$



$$K_a = \frac{x(0.158745 + x)}{(0.15261 - x)} = 6.2 \times 10^{-8} \quad \leftarrow \text{this is } K_{a2} \text{ of } \text{H}_3\text{PO}_4$$

ass. $x \ll .153, .158$

$$\frac{x(0.158745)}{0.15261} = 6.2 \times 10^{-8}$$

$$x = [\text{H}^+] = 5.9(6) \times 10^{-8} \text{ M}$$

$\text{pH} = 7.22$

32

Want: Buffer w/ pH = 5.00

- Have:
- 0.10 M $\text{HCOOH} \leftarrow K_a = 1.8 \times 10^{-4}$ (from p. 1062) $\text{p}K_a = -\log(1.8 \times 10^{-4})$
 $\text{p}K_a = 3.74$
 - 0.10 M HCOONa
 - 0.10 M $\text{CH}_3\text{COOH} \leftarrow K_a = 1.8 \times 10^{-5}$ $\text{p}K_a = 4.74$
 - 0.10 M CH_3COONa
 - 0.10 M $\text{HCN} \leftarrow K_a = 4.9 \times 10^{-10}$ $\text{p}K_a = 9.31$
 - 0.10 M NaCN

Since we want pH = 5.00, we should choose an acid with the $\text{p}K_a$ closest to 5.00, so choose CH_3COOH . We also need its conj. base, so we'll choose

CH_3COOH (acetic acid) and $\text{CH}_3\text{COONa}/\text{NaCH}_3\text{COO}$ (sodium acetate)

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad 1.8 \times 10^{-5} = \frac{[10^{-5.00}][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8$$

Both solutions are 0.10 M, so the ratio of molarities will be the same as the ratio of mL we use. We are supposed to use 1000 mL total.

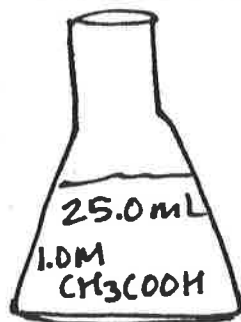
Solve

$$\begin{cases} [\text{CH}_3\text{COO}^-] = 1.8 [\text{CH}_3\text{COOH}] \\ V_{\text{CH}_3\text{COO}^-} = 1.8 V_{\text{CH}_3\text{COOH}} \\ V_{\text{CH}_3\text{COO}^-} + V_{\text{CH}_3\text{COOH}} = 1000 \end{cases} \rightarrow \begin{cases} 1.8 V_{\text{CH}_3\text{COOH}} + V_{\text{CH}_3\text{COOH}} = 1000 \\ 2.8 V_{\text{CH}_3\text{COOH}} = 1000 \\ V_{\text{CH}_3\text{COOH}} = 357 \text{ mL} \\ V_{\text{CH}_3\text{COO}^-} = 643 \text{ mL} \end{cases}$$

OR 2 SF OK too.



35



← Both acids are titrated
w/ 0.100 M NaOH

← acetic acid, a weak acid.

TRUE/FALSE?

- (a) The HNO_3 needs a larger volume of NaOH to reach equivalence pt.

False. Each flask contains .025 moles of a monoprotic acid, so each will require .025 mole NaOH to reach EQ PT. (or each requires 250 mL of NaOH to reach EQ PT)

- (b) The pH at EQ PT will be lower for HNO_3 than it will be for CH_3COOH .

TRUE. HNO_3 is a strong acid, so when titrated with a strong base, EQ PT will be 7.0.

Since CH_3COOH is a weak acid, it will be basic at EQ PT when titrated w/ strong base, so $\text{pH} > 7$.

- (c) phenolphthalein would be suitable for both titrations.

TRUE. phenolphthalein changes at pH 8-10, which is right around the EQ pt for acetic acid, and still in the steep part of the titration curve for HNO_3 . It will change color within a small fraction of a mL (of NaOH) of eq. pt.

36

- (a) The pH at beginning of each titration is same.

FALSE. Initial pH will be lower for HNO_3 .

$$\text{HNO}_3 \text{ pH} = -\log(1.0) = 0 \quad \leftarrow \text{based on } K_a \text{ calc.}$$

$$\text{CH}_3\text{COOH} \text{ pH} = -\log(.0042) = 2.37$$

- (b) The titration curves are essentially the same after the eq. pt.

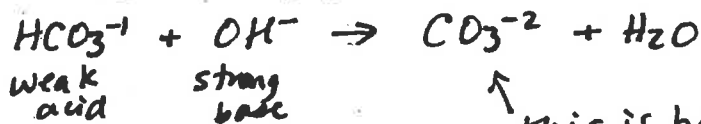
True .. depending on what "essentially" means. ^{from excess NaOH;} past the equivalence pt the " HNO_3 " flask contains OH^- ions (a strong base), and " acetic acid " has the excess OH^- ions (from NaOH) plus the $\text{C}_2\text{H}_3\text{O}_2^-$ is a weak base, which will produce a very tiny bit more OH^- , but to a couple SF they will be identical

- (c) Methyl Red is an ok indicator for each. FALSE. It changes at $\text{pH} \approx 4.5$ to 6, which is fine for the HNO_3 , since it's close to EQ PT of 7. but it will change too soon for acetic acid, which has an EQ PT of around 9.

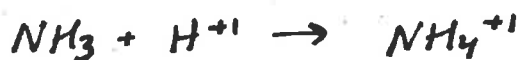
37 predict pH @ EQ PT

(a) NaHCO_3 titrated w/ NaOH

↑
this is amphoteric (the HCO_3^- ion can accept or donate a proton) but since it is reacting w/ NaOH , a strong base, the NaHCO_3 (HCO_3^-) will act as the acid.

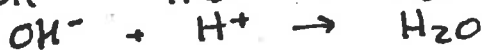


↑ since it's the c. base of a weak acid!
this is basic. since a basic ion, carbonate, is present at EQ pt, $\text{pH} > 7$ at EQ PT.

(b) NH_3 titrated w/ HCl 

↑ weak base

$\text{pH} < 7$ at EQ PT
since NH_4^+ , a weak acid, is present

(c) KOH titrated w/ HBr strong base + strong acid so $\text{pH} = 7$ at eq. pt.

only K^+ and Br^- (and H_2O) present at eq. pt. K^+ and Br^- and H_2O are all neutral.

42 How many mL 0.105 M HCl required to reach EQ PT if titrating these solutions.(a) 45.0 mL of 0.0950 M NaOH

Moles acid = moles base at E.P.

$$M_a V_a = M_b V_b$$

$$(.105 \text{ M}) V_a = (.0950 \text{ M}) (45.0 \text{ mL})$$

$$V_a = 40.7 \text{ mL HCl}$$

(b) 22.5 mL of .118 M NH_3

$$M_a V_a = M_b V_b$$

$$(.105 \text{ M}) V_a = (.118 \text{ M}) (22.5 \text{ mL})$$

$$V_a = 25.3 \text{ mL}$$

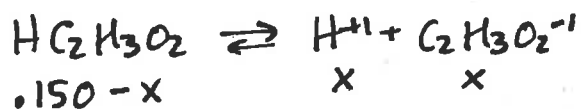
(c) 125.0 mL of soln containing 1.35 g NaOH per Liter

$$M_a V_a = M_b V_b \quad (.105 \text{ M}) V_a = \left(\frac{1.35 \text{ g}}{39.9971 \frac{\text{g}}{\text{mole}}} \right) \left(\frac{125.0 \text{ mL}}{1.00 \text{ L}} \right)$$

$$V_a = 40.2 \text{ mL}$$

45 All right! Titrating 35.0 mL of 0.150 M acetic acid ($\text{C}_2\text{H}_3\text{O}_2\text{H} / \text{HC}_2\text{H}_3\text{O}_2$) with 0.150 M NaOH! Calculate pH after _____ mL NaOH added!

(a) 0.0 mL NaOH added. So, finding pH of 0.150 M $\text{HC}_2\text{H}_3\text{O}_2$



$$K_a = \frac{x^2}{.150 - x} = 1.8 \times 10^{-5}$$

assume $x \ll 0.150$

$$x = 0.001643$$

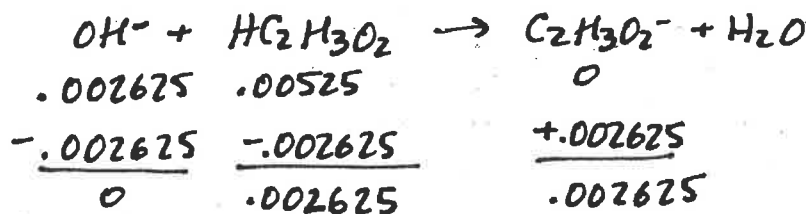
plug back in $\frac{x^2}{.150 - .001643} = 1.8 \times 10^{-5}$

$$x = .0016341$$

and... $x = .0016342 \checkmark = [\text{H}^+]$

$$\text{pH} = -\log(.0016342) = \boxed{2.79}$$

(b) 17.5 mL $(.0350 \text{ L})(.150 \text{ M}) = .00525$ moles $\text{HC}_2\text{H}_3\text{O}_2$
 $(.0175 \text{ L})(.150 \text{ M}) = .002625$ moles NaOH

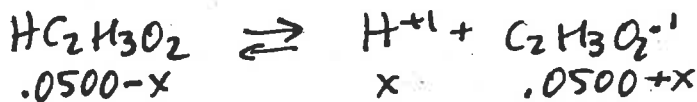


Assume volume additive..

$$35.0 \text{ mL} + 17.5 \text{ mL} = 52.5 \text{ mL}$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-] = \frac{.002625 \text{ mol}}{.0525 \text{ L}} = 0.0500 \text{ M}$$

K_a :



$$K_a = \frac{x(.0500 + x)}{.0500 - x} = 1.8 \times 10^{-5}$$

assume $x \ll .0500$ so $\frac{x(.0500)}{.0500} = 1.8 \times 10^{-5}$

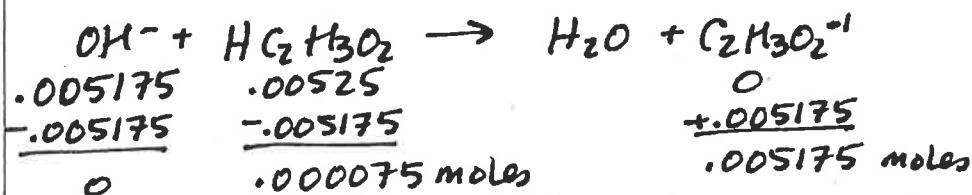
$$x = 1.8 \times 10^{-5} \quad \text{pH} = -\log [\text{H}^+] = -\log (1.8 \times 10^{-5}) = \boxed{4.74}$$

← or instead you could now say
 50/50 buffer so
 $\text{pH} = \text{p}K_a$
 $= -\log(1.8 \times 10^{-5})$
 $= 4.74!$

Cont'd, next page!

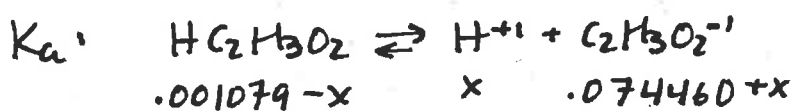
(45) cont'd (c) 34.5 mL NaOH added

$$(0.0345 \text{ L})(.150 \text{ M}) = 0.005175 \text{ mole NaOH}$$



$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{.000075 \text{ mole}}{.0695 \text{ L}} = .001079 \text{ M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{.005175 \text{ mole}}{.0695 \text{ L}} = .074460 \text{ M}$$



$$K_a = \frac{x(.074460 + x)}{(.001079 - x)} = 1.8 \times 10^{-5}$$

assume $x \ll .001079, .074460$

$$\frac{x(.074460)}{.001079} = 1.8 \times 10^{-5}$$

$$x = 2.608 \times 10^{-7} \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log(2.608 \times 10^{-7})$$

$$\text{pH} = 6.58$$

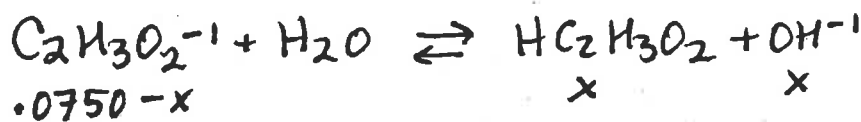
(d) 35.0 mL NaOH added

This is the equivalence pt since flask now contains .00525 moles $\text{HC}_2\text{H}_3\text{O}_2$ plus .00525 moles NaOH. These will react to form .00525 moles of $\text{NaC}_2\text{H}_3\text{O}_2$ (+ H_2O)

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{.00525 \text{ mole}}{.0700 \text{ L}} = 0.0750 \text{ M}$$

$$K_b \text{ of } \text{C}_2\text{H}_3\text{O}_2^- = \frac{K_w}{K_a(\text{HC}_2\text{H}_3\text{O}_2)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5(6) \times 10^{-10}$$

$K_b:$



$$K_b = \frac{x^2}{.0750 - x} = 5.5(6) \times 10^{-10}$$

(assume $x \ll .0750$)

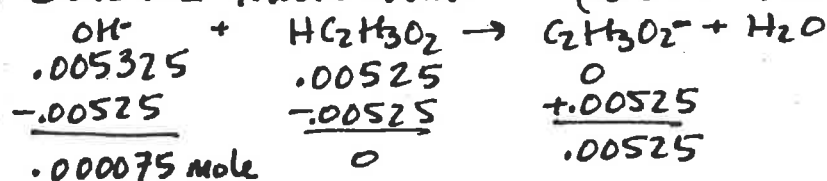
$$x = 6.455 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = 5.19$$

$$\text{pH} = 14 - \text{pOH} = 8.81$$

cont'd →

(45) cont'd ... again ...

(e) 35.5 mL NaOH added $(.0355\text{L})(.150\text{M}) = .005325\text{ mole}$ 

↑
 we have a strong base (OH^-) and a weak base ($\text{C}_2\text{H}_3\text{O}_2^-$)
 lets ignore the weak base! it has a low K_b (5.6×10^{-10}) and there
 is already OH^- present
 so "common ion effect"
 will reduce acetate's
 ability to create
 more OH^- . it will
 only contribute \approx
 $4 \times 10^{-8}\text{ M}$ more OH^- !

$$[\text{OH}^-] = \frac{.000075\text{ mole}}{.0705\text{ L}} = .0010638\text{ M}$$

$$\text{pOH} = -\log(.0010638) = 2.97$$

$$\text{pH} = 14 - \text{pOH} = \boxed{11.03}$$

(f) 50.0 mL NaOH added $(.0500\text{L})(.150\text{M}) = .00750\text{ moles}$

we are past the equiv. point and know from (e) that
 we only need to deal w/ the excess OH^- concentration,
 not the $\text{C}_2\text{H}_3\text{O}_2^-$ concentration.

$$.00750\text{ moles OH}^- - \left(\begin{array}{l} .00525\text{ moles OH}^- \\ \text{needed to react} \\ \text{w/ .00525 moles acid} \end{array} \right) = .00225\text{ moles OH}^- \text{ in excess}$$

$$\frac{.00225\text{ moles OH}^-}{.0850\text{ L}} = 0.02647\text{ M OH}^-$$

$$\text{pOH} = -\log(.02647) = 1.58 \quad (1.5772)$$

$$\text{pH} = 14 - \text{pOH} = \boxed{12.42}$$

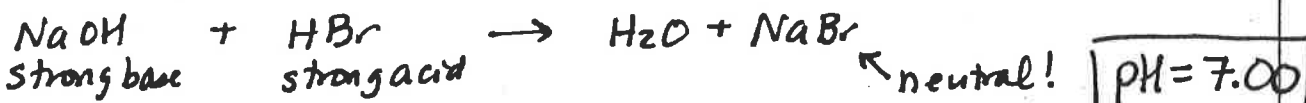
Note: (e) and (f) could actually be 3 sig figs (if volumes really
 are additive)
 since you aren't limited by the K_a value SF (1.8×10^{-5})

but if you want to do 3 SF you'd need to use
 $K_w = 1.01 \times 10^{-14}$ so $\text{pH} + \text{pOH} = 13.995(68)$.

(not 14.00000...)

if so, (f) would be
 $\text{pH} = 13.995(68) - 1.5772 = \boxed{12.418}$ awesome.

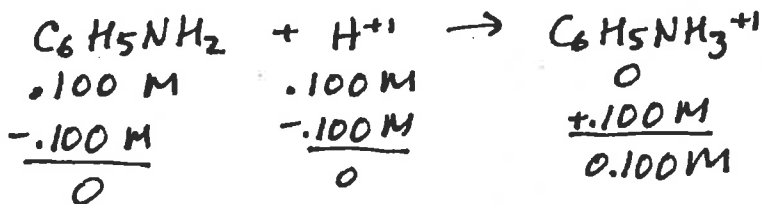
47 (a) EQ PT pH if 0.200 M NaOH titrated w/ 0.200 M HBr



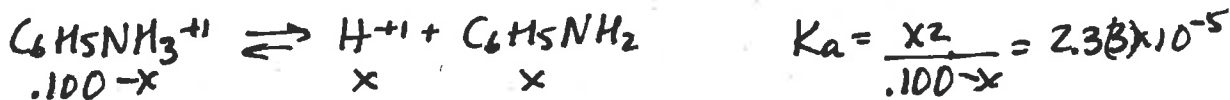
(b) 0.200 M aniline ($\text{C}_6\text{H}_5\text{NH}_2$) + .200 M HBr
 weak base strong acid

The equivalence point will be acidic.

Since molarities are equal, equal volumes of acid and base will have been "added" at EQ Pt, so acc to $M_1V_1 = M_2V_2$, both molarities will cut in half to .100 M.



$$K_a(\text{C}_6\text{H}_5\text{NH}_3^+) = \frac{K_w}{K_b(\text{C}_6\text{H}_5\text{NH}_2)} = \frac{10^{-14}}{4.3 \times 10^{-10}} = 2.33 \times 10^{-5}$$



$$K_a = \frac{x^2}{.100 - x} = 2.33 \times 10^{-5}$$

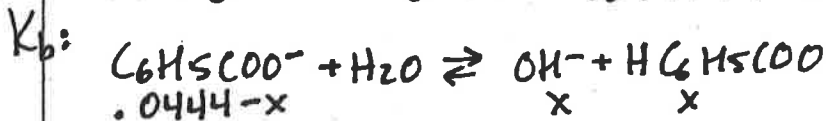
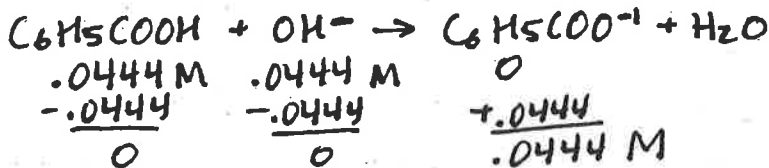
ass. $x \ll .100$

$$x = .00152 \text{ M}$$

$$\text{pH} = -\log(.00152) = \boxed{2.82}$$

48 (a) .100 M HBr titrated w/ .080 M NaOH
 as in 47a, this will be neutral at EQ PT. pH = 7.00

(c) 0.100 M Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$ titrated w/ 0.080 M NaOH
 a weak acid is titrated w/ a strong base, so pH will be basic at equiv. pt; $\text{C}_6\text{H}_5\text{COO}^-$ is basic..



$$K_b = \frac{x^2}{.0444 - x} = \frac{K_w}{K_a(\text{C}_6\text{H}_5\text{COOH})} = \frac{10^{-14}}{6.3 \times 10^{-5}} = 1.587 \times 10^{-10}$$

ass. $x \ll .0444$ $\frac{x^2}{.0444} = 1.587 \times 10^{-10}$

$$x = 2.66 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pH} = 14 + \log(2.66 \times 10^{-6}) = \boxed{8.42}$$

To get the .0444 M:
 Say we had 1.00 L of benzoic acid
 acc to $M_A V_A = M_B V_B$ we'd need
 1.25 L of NaOH to reach EQPT.
 So $V_{\text{TOTAL}} = 2.25 \text{ L of EP}$
 $.100 \text{ M} \left(\frac{1.00 \text{ L}}{2.25 \text{ L}} \right) = 0.0444 \text{ M}$

59

Calculate solubility of $Mn(OH)_2$ in g/L when buffered at (a) pH = 7.0 (b) pH = 9.5 (c) pH = 11.8

From Appendix D3, page 1063, K_{sp} of $Mn(OH)_2 = 1.6 \times 10^{-13}$
molar mass of $Mn(OH)_2 = 88.9526$ g/mole

$$K_{sp} = [Mn^{+2}][OH^-]^2$$

(a) at pH = 7.0 pOH = 14 - pH = 7.0

$$[OH^-] = 10^{-7.0} = 1. \times 10^{-7}$$

$$[Mn^{+2}](1 \times 10^{-7})^2 = 1.6 \times 10^{-13}$$

$$[Mn^{+2}]_{max} = 16 M = \text{molar solubility of } Mn(OH)_2 \text{ since there is } 1 Mn^{+2} / 1 Mn(OH)_2$$

(assuming Mn^{+2} is still this soluble with whatever anions are in the buffer solution!)

$$(16 M)(88.9526 \frac{g}{mole}) = \underline{1423 g/L} \quad (\text{or really } 1000 g/L \text{ w/ the SF given})$$

(b) at pH = 9.5, pOH = 14 - 9.5 = 4.5, so $[OH^-] = 10^{-4.5}$

$$[Mn^{+2}](10^{-4.5})^2 = 1.6 \times 10^{-13}$$

$$[Mn^{+2}]_{max} = 0.00016 M$$

$$(0.00016 M)(88.9526 g/mole) = \boxed{0.014 g/L} \quad (\text{or really, 1 SF})$$

(c) at pH 11.8, pOH = 14 - 11.8 = 2.2

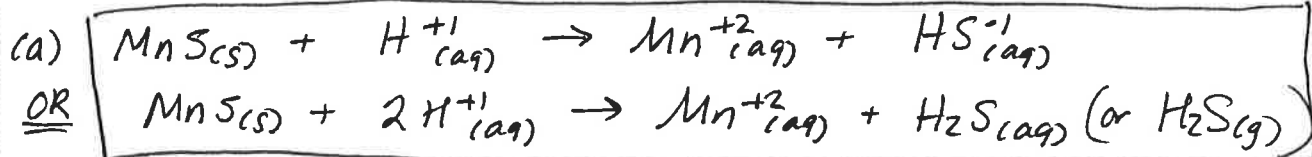
$$[Mn^{+2}](10^{-2.2})^2 = 1.6 \times 10^{-13}$$

$$[Mn^{+2}]_{max} = 4.02 \times 10^{-9} M$$

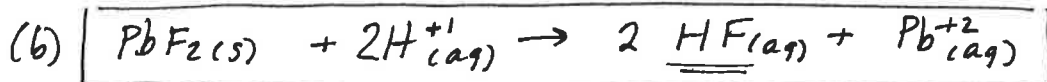
$$(4.02 \times 10^{-9} M)(88.9526 g/mole) = \boxed{3.6 \times 10^{-7} g/L} \quad (\text{really, 1 SF})$$

Chapter 17

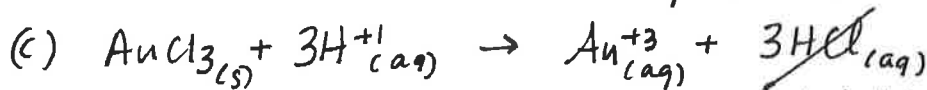
62 Write net ionic eqn for rxn of each salt (if any) with acid
 (a) MnS (b) PbF_2 (c) $AuCl_3$ (d) $Hg_2C_2O_4$ (e) $CuBr$



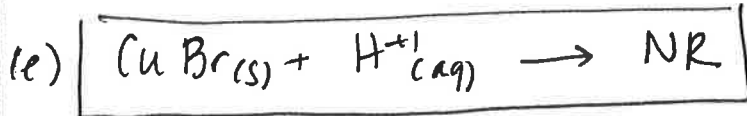
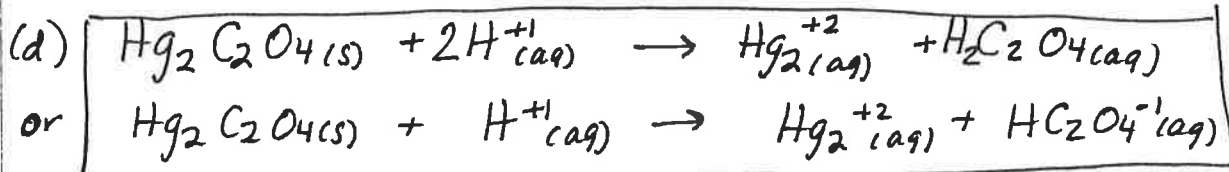
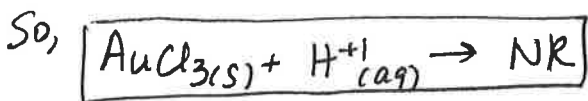
This works because H_2S and HS^- are weak acids, so they will not significantly ionize / split up into $H^+/S^{2-}/HS^-$



\uparrow
 weak acid, so it doesn't split (much) back up into H^+/F^-



but this is a strong acid, so it will split back up into H^+ and Cl^- . So H^+ will cancel, and the rxn will just be the regular K_{sp} equation.



Since HBr is a strong acid and will split up 100% (same idea as (c))

69 Calc. minimum pH needed to precipitate $Mn(OH)_2$ so completely that the remaining $[Mn^{2+}]$ is less than $1 \mu g$ per liter.

$$[Mn^{2+}] = (1 \times 10^{-6} g) \left(\frac{1 \text{ mole}}{54.938 g} \right) = 1.82 \times 10^{-8} M \text{ } Mn^{2+}$$

$$K_{sp} = [Mn^{2+}][OH^-]^2 = 1.6 \times 10^{-13} \text{ (from page 1063)}$$

$$(1.82 \times 10^{-8} M) [OH^-]^2 = 1.6 \times 10^{-13}$$

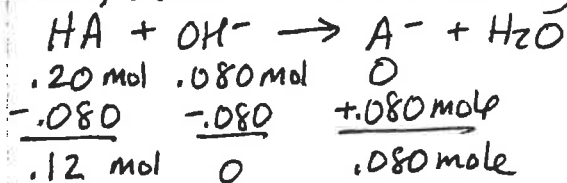
$$[OH^-] = 2.9648 \times 10^{-3} M$$

$$pOH = 2.53, \text{ } pH = 14 - pOH = 11.47 \rightarrow \boxed{11.5}$$

pH must stay ^{at} above 11.5 to precipitate the $Mn(OH)_2$ enough. the higher the pH, the more OH^- , so the less the Mn^{2+} can dissolve.

- 91) "HA" combined w/NaOH: 0.20 mole HA + .080 M NaOH in 1.0 L total
 (a) if pH = 4.80, find the pKa of the acid.

First, react the NaOH (strong base) w/ the acid.



$$[\text{HA}] = \frac{.12 \text{ mol}}{1.0 \text{ L}} = 0.12 \text{ M}$$

$$[\text{A}^-] = \frac{.080 \text{ mole}}{1.0 \text{ L}} = 0.080 \text{ M}$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.80} = 1.5(8) \times 10^{-5} \text{ M}$$

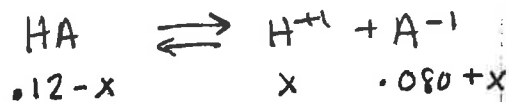
Note: Since neglecting x is valid for part (a), you could also use the Henderson Hasselbach equation:

$$\text{pH} = \text{pKa} + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$4.80 = \text{pKa} + \log \left(\frac{0.080}{0.12} \right)$$

$$\boxed{\text{pKa} = 4.98}$$

use these values to do a Ka:



$$\begin{array}{ccc} .12 - x & x & .080 + x \end{array}$$

$$\text{but } x = 1.58 \times 10^{-5} \text{ M !}$$

$$K_a = \frac{[x][.080 + x]}{[.12 - x]}$$

$$K_a = \frac{(1.58 \times 10^{-5})(.080 + 1.58 \times 10^{-5})}{.12 - 1.58 \times 10^{-5}}$$

or you could just "neglect" the 1.58×10^{-5} since it is $\ll .12$!

$$\begin{aligned} K_a &= 1.0(5) \times 10^{-5} \\ \text{pKa} &= -\log(1.05 \times 10^{-5}) \\ \boxed{\text{pKa} = 4.98} \end{aligned}$$

- (b) How many moles of OH^- (NaOH) must be added to change the pH to 5.00?

$$K_a = 1.0(5) \times 10^{-5} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{but } [\text{H}^+] = 10^{-5.00}$$

$$(1.05 \times 10^{-5}) = \frac{10^{-5.00}[\text{A}^-]}{[\text{HA}]}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{1.0(5) \times 10^{-5}}{1.0 \times 10^{-5}} = 1.0(5)$$

$$[\text{A}^-] = \frac{.080 \text{ mole} + B}{1.0 \text{ L}}$$

$$[\text{HA}] = \frac{.12 \text{ mole} - B}{1.0 \text{ L}}$$

where B = the moles of Base added



Since OH^- will convert HA into A^-

$$\text{so } \frac{(.080 + B)}{(.12 - B)} = 1.0(5)$$

$$\begin{aligned} .080 + B &= 1.05(.12 - B) \\ .080 + B &= 0.126 - 1.05B \\ 2.05B &= .046 \end{aligned}$$

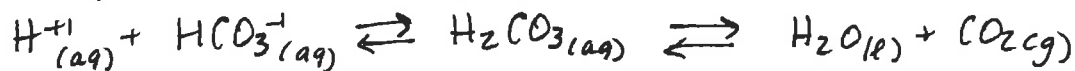
$$B = 0.0224 \text{ moles base must be added}$$

Though you lose a SF in the subtraction so really

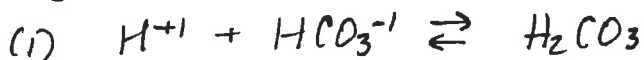
$$\boxed{B = .02 \text{ moles NaOH}}$$

95 Anxiety \rightarrow rapid breathing \rightarrow alkalosis (increase in blood pH)

(a) explain why rapid breathing can lead to alkalosis.
use equation # 17.10. (page 713):



I'm gonna split this into two equations:

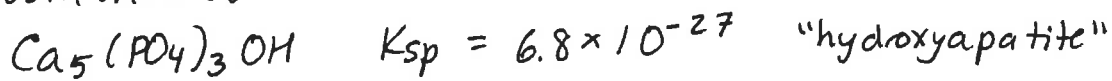


Rapid breathing means that $\text{CO}_2(g)$ will be able to leave your blood at a higher rate. The more breaths per minute, the lower the partial pressure of $\text{CO}_2(g)$ in your lungs, so the less soluble CO_2 is in blood, according to Henry's Law (the solubility of a gas is proportional to the gas's partial pressure) as $[\text{CO}_2(g)]$ in lungs decreases, rxn (2) shifts right, which will cause $[\text{H}_2\text{CO}_3]$ to drop as it is consumed in rxn (2) as $[\text{H}_2\text{CO}_3]$ decreases, rxn (1) will shift right, so H^+ will be consumed. as $[\text{H}^+]$ decreases, $[\text{OH}^-]$ increases, so blood pH will increase (become more basic/alkali).

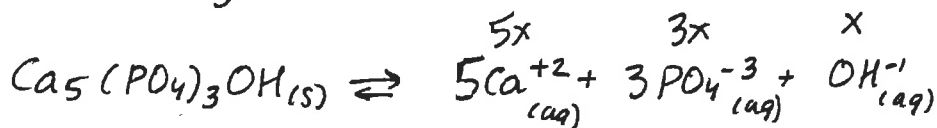
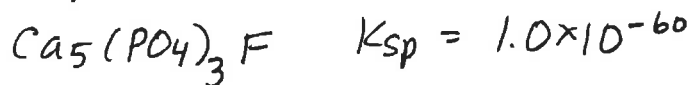
(b) Why does it help to breathe in a paper bag?

If you breathe in a paper bag, the "air" in the bag will have a higher concentration of CO_2 than normal air, since it will contain CO_2 from you! the higher the partial pressure of CO_2 in the air you breathe, and in your lungs, the more carbonic acid and H^+ you will have in your blood; keeping CO_2 levels high keeps rxns (1) and (2) shifted left.

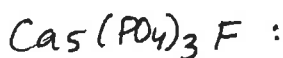
98 Tooth enamel!



or, fluoride ion (from toothpaste, fluoride pills, fluoridated H₂O...) can replace the OH⁻ to form "fluoroapatite":

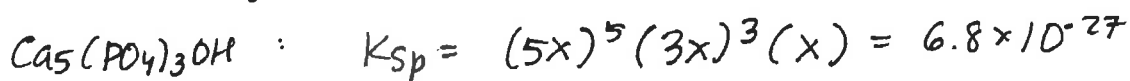


$$K_{sp} = [\text{Ca}^{+2}]^5 [\text{PO}_4^{-3}]^3 [\text{OH}^-] = 6.8 \times 10^{-27}$$



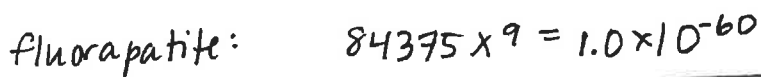
$$K_{sp} = [\text{Ca}^{+2}]^5 [\text{PO}_4^{-3}]^3 [\text{F}^-] = 1.0 \times 10^{-60}$$

molar solubility:



$$84375 x^9 = 6.8 \times 10^{-27}$$

$$x = 0.00035 \text{ M} \quad \text{Ca}_5(\text{PO}_4)_3\text{OH}$$



$$x = 6.1 \times 10^{-8} \text{ M} \quad \text{Ca}_5(\text{PO}_4)_3\text{F}$$

wow! its almost as if replacing OH⁻ with F⁻ might make your tooth enamel less soluble! 😊

also, replacing OH⁻ with F⁻ decreases the solubility of enamel in acids...

