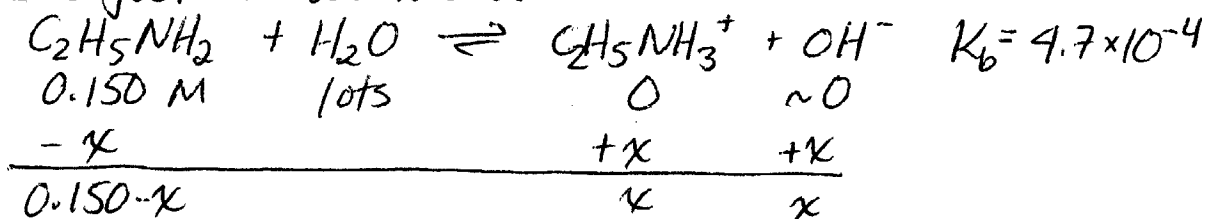


Answers to Practice Problems (Buffers)

1. a) initially: no HCl added.
have just a weak base.



$$K_b = \frac{x^2}{0.150 - x} = 4.7 \times 10^{-4} \quad x = \sqrt{(0.150)(4.7 \times 10^{-4})}$$

↙ neglect x

$$x = 8.4 \times 10^{-3} \text{ M}$$

can't neglect x!

$$x = \sqrt{(0.150 - 8.4 \times 10^{-3})(4.7 \times 10^{-4})} = 8.16 \times 10^{-3} \text{ M}$$

$$x = \sqrt{(0.150 - 8.16 \times 10^{-3})(4.7 \times 10^{-4})} = 8.16 \times 10^{-3} \text{ M} \quad \text{OH}^-$$

pOH = 2.09

pH = 11.91

- b) at the halfway point, ~~the~~ $[\text{C}_2\text{H}_5\text{NH}_2] = [\text{C}_2\text{H}_5\text{NH}_3^+]$

$$K_b = \frac{[\text{OH}^-][\text{C}_2\text{H}_5\text{NH}_3^+]}{[\text{C}_2\text{H}_5\text{NH}_2]} \quad \text{so } K_b = [\text{OH}^-] = 4.7 \times 10^{-4}$$

pOH = 3.33

pH = 10.67

- c) at the endpoint: all $\text{C}_2\text{H}_5\text{NH}_2$ has been converted to $\text{C}_2\text{H}_5\text{NH}_3^+$.

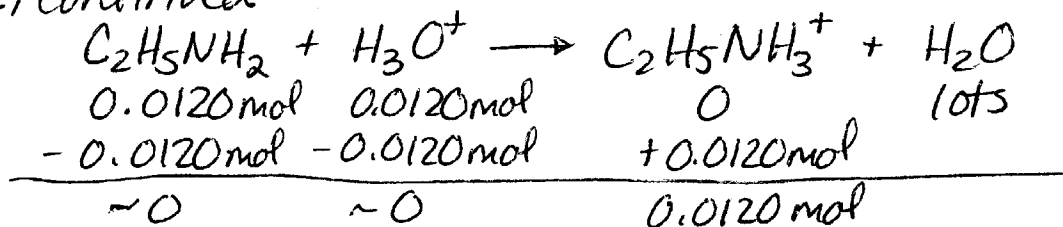
initial # moles $\text{C}_2\text{H}_5\text{NH}_2$:

$$(0.0800 \text{ L}) \left(\frac{0.150 \text{ mol}}{\text{L}} \right) = 0.0120 \text{ mol } \text{C}_2\text{H}_5\text{NH}_2$$

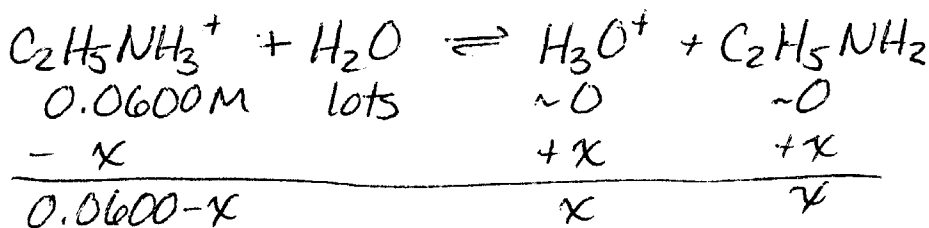
so 0.0120 mol HCl has been added at the endpoint (because the reaction is 1:1)

$$\text{so } (0.0120 \text{ mol HCl}) \left(\frac{\text{L}}{0.100 \text{ mol HCl}} \right) = 0.120 \text{ L HCl added} \quad (120 \text{ mL})$$

1 c) continued



divide by V_{tot} : $80 \text{ mL} + 120 \text{ mL} = 200 \text{ mL}$
 $\frac{0.0120 \text{ mol}}{0.200 \text{ L}} = 0.0600 \text{ M } \text{C}_2\text{H}_5\text{NH}_3^+$
 this is a weak acid.

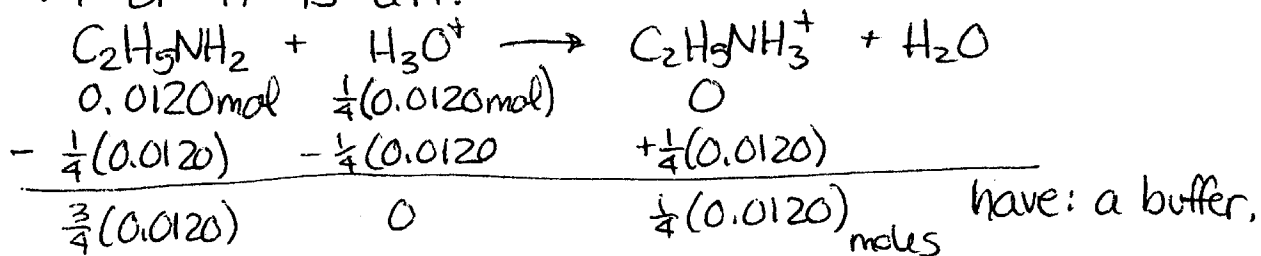


$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.13 \times 10^{-11} = \frac{x^2}{0.0600 - x}$$

so $x = \sqrt{(0.0600)(2.13 \times 10^{-11})} = 1.13 \times 10^{-6} \text{ M } \text{H}_3\text{O}^+$ ↑ neglect x

pH = 5.95

d) at $\frac{1}{4}$ completion: $\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O}$
 $\frac{1}{4}$ of the $\text{C}_2\text{H}_5\text{NH}_2$ has been converted to $\text{C}_2\text{H}_5\text{NH}_3^+$.
 $\frac{3}{4}$ of it is left.



ratio of ~~B~~ B to HB^+ is important!

ratio is 3 B : 1 HB^+ at this point.

$$K_b = \frac{[\text{OH}^-]}{\left(\frac{\text{mol } \text{HB}^+}{\text{mol B}}\right)} \quad [\text{OH}^-] = 4.7 \times 10^{-9} \left(\frac{\text{mol B}}{\text{mol } \text{HB}^+}\right)$$

1d continued

$$[\text{OH}^-] = 4.7 \times 10^{-4} \left(\frac{3}{1} \right) = 1.4 \times 10^{-3}$$

$$\begin{aligned} \text{pOH} &= 2.85 \\ \text{pH} &= 11.15 \end{aligned}$$

you could do this by calculating the molarity of B and HB^+ - the result would be the same, but it's more work.

Need to divide by the new total volume - but how much HCl was added?

$$\frac{1}{4} (0.0120 \text{ mol}) = 0.00300 \text{ mol}$$

$$(0.00300 \text{ mol}) \left(\frac{\text{L}}{.100 \text{ mol}} \right) = 0.0300 \text{ L} = 30.0 \text{ mL} \quad (\text{original: } 80 \text{ mL total } 110 \text{ mL})$$

$$[\text{B}] = \frac{\frac{3}{4} (0.0120 \text{ mol})}{0.110 \text{ L}} = 0.0818 \text{ M B}$$

$$[\text{HB}^+] = \frac{\frac{1}{4} (0.0120 \text{ mol})}{0.110 \text{ L}} = 0.0273 \text{ M HB}^+$$

then

$$[\text{OH}^-] = K_b \frac{[\text{B}]}{[\text{HB}^+]} = 4.7 \times 10^{-4} \left(\frac{0.0818 \text{ M}}{0.0273 \text{ M}} \right)$$

$$[\text{OH}^-] = 1.4 \times 10^{-4} \quad \begin{aligned} \text{pOH} &= 2.85 \\ \text{pH} &= 11.15 \end{aligned}$$

Moral: look for shortcuts!

e) at $\frac{3}{4}$ completion.

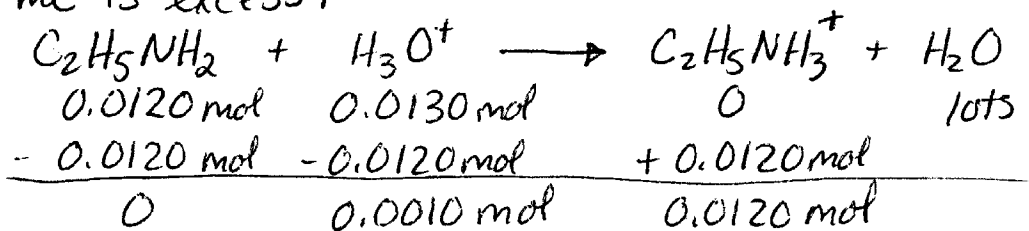
at this point, $\frac{3}{4}$ of the B has been converted to HB^+ , and $\frac{1}{4}$ of it remains.

$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} \quad [\text{OH}^-] = K_b \left(\frac{\text{mol B}}{\text{mol HB}^+} \right) = 4.7 \times 10^{-4} \left(\frac{(\frac{1}{4} \times) \text{B}}{(\frac{3}{4} \times) \text{HB}^+} \right)$$

$$[\text{OH}^-] = K_b \left(\frac{1}{3} \right) = 1.57 \times 10^{-4}$$

$$\text{pOH} = 3.805 \quad \boxed{\text{pH} = 10.19}$$

f) 10.0 mL HCl beyond the endpoint.
at the endpoint, we have added 120 mL HCl
so here we have added 130 mL HCl.
120 mL is used to convert all of the B to HB^+
10 mL is excess:



@ end: have $\text{C}_2\text{H}_5\text{NH}_3^+$, a weak acid
and H_3O^+ , a strong acid!

the 0.0010 mol H_3O^+ present will overpower the
 H_3O^+ contribution from the dissociation of $\text{C}_2\text{H}_5\text{NH}_3^+$.
(check: look @ 1c: $[\text{H}^+]$ was $1.1 \times 10^{-6} \text{ M}$. It will
be even less in the presence of a common ion.
so this contribution is negligible in comparison.)

$$V_{\text{total}} = 80 \text{ mL} + 130 \text{ mL} = 210 \text{ mL}$$

$$\frac{0.0010 \text{ mol } \text{H}_3\text{O}^+}{.210 \text{ L}} = 0.00476 \text{ M } \text{H}_3\text{O}^+$$

$$\boxed{\text{pH} = 2.32}$$

2. Volume of HCl needed:

we did some of these already.

to reach the endpoint, need # mol HCl = # mol
base present initially.

0.0120 mol B present \Rightarrow 0.0120 mol HCl needed
to react with it. This corresponds to 120 mL.

(see prob 1c).

at the halfway point, it will take $\frac{1}{2}$ of this HCl. etc.

a) 0 mL HCl

d) $\frac{1}{2}(120) = 30 \text{ mL HCl}$

b) 60 mL HCl

e) 90 mL HCl

c) 120 mL HCl

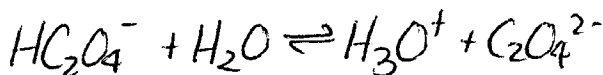
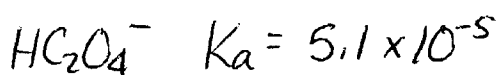
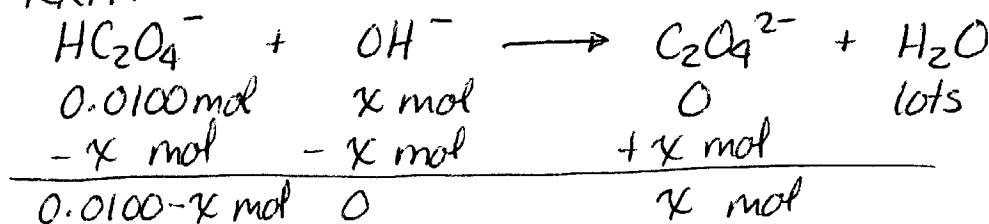
f) 130 mL HCl

3. Appropriate indicator: would change color at a pH near the equivalence point.

see 1c: eq. point pH = 5.95 so choose one that changes around pH 6 - actually one that starts changing around pH 6 (or lower pH)

Methyl Red would probably be good - changes 4-6. ^{pH:}

4. Rxn:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]}$$

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{5.1 \times 10^{-5}}{2.0 \times 10^{-5}} = \frac{2.55}{1}$$

buffer!

(ratio is between 1:10 and 10:1)

$$\text{pH} = 4.70, \text{H}^+ = 2.0 \times 10^{-5} \text{ M}$$

$$\frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = \frac{\text{moles C}_2\text{O}_4^{2-}}{\text{moles HC}_2\text{O}_4^-} = \frac{2.55}{1}$$

see chart above: $x = \# \text{ moles OH}^- \text{ added.}$

$$\frac{\text{moles C}_2\text{O}_4^{2-}}{\text{moles HC}_2\text{O}_4^-} = \frac{x}{\frac{0.0100 - x}{0.0100 - x}} = \frac{2.55}{1}$$

$$x = 2.55(0.0100 - x)$$

$$x = 0.0255 - 2.55x$$

$$3.55x = 0.0255$$

$$x = 0.00718 \text{ moles OH}^- \text{ added!}$$

$$\left(0.00718 \text{ mol OH}^- \right) \left(\frac{1 \text{ L}}{0.120 \text{ mol OH}^-} \right)$$

$$\rightarrow = 0.060 \text{ L } 0.060 \text{ L}$$

$$= \boxed{60 \text{ mL } 0.120 \text{ M NaOH}}$$

*

5. a) Add NaNO_2 to HNO_2 .
at first: pH is low (acidic). As you add NaNO_2 , you are adding the conjugate base. pH will get higher (get more basic).

b) Add NaNO_3 to HNO_3
 HNO_3 is a strong acid. pH starts low.
 NaNO_3 is neutral. adding it will not affect the pH.

The difference: HNO_2 is a weak acid. HNO_3 is a strong acid. The conjugate base of a strong acid is neutral (has no attraction for H^+ ions).

$$6. (1.51 \text{ g NH}_3) \left(\frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \right) = 0.08836 \text{ mol NH}_3$$

$$(3.85 \text{ g (NH}_4)_2\text{SO}_4) \left(\frac{1 \text{ mol}}{132.26 \text{ g}} \right) = 0.02911 \text{ mol (NH}_4)_2\text{SO}_4$$

so $2 \times \text{this} =$
 $0.058217 \text{ mol NH}_4^+$

a) a buffer.

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} \quad [\text{OH}^-] = K_b \left(\frac{\text{mol NH}_3}{\text{mol NH}_4^+} \right)$$

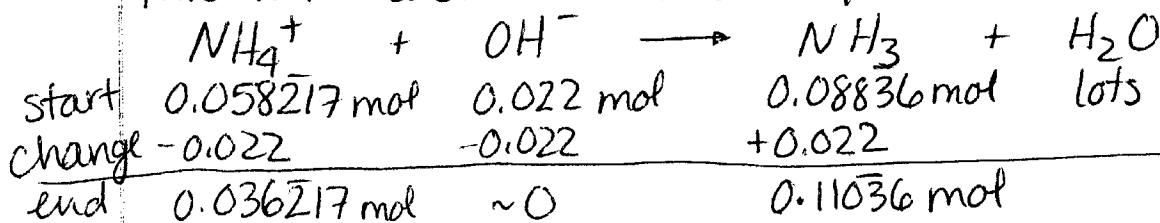
$$[\text{OH}^-] = 1.8 \times 10^{-5} \left(\frac{0.08836 \text{ mol NH}_3}{0.058217 \text{ mol NH}_4^+} \right) = 2.73 \times 10^{-5} \text{ M OH}^-$$

$$\text{pOH} = 4.56$$

$$\text{pH} = 9.44$$

b) add $0.88 \text{ g NaOH} \quad (0.88 \text{ g}) \left(\frac{1 \text{ mol}}{40.00 \text{ g}} \right) = 0.022 \text{ mol NaOH}$

this will react with the NH_4^+ .



6b) continued
have - another buffer.

$$[\text{OH}^-] = K_b \left(\frac{\text{mol NH}_3}{\text{mol NH}_4^+} \right) = 1.8 \times 10^{-5} \left(\frac{0.11036 \text{ mol NH}_3}{0.036217 \text{ mol NH}_4^+} \right)$$

$$[\text{OH}^-] = 5.5 \times 10^{-5} \text{ M} \quad \text{pOH} = 4.26$$

$\text{pH} = 9.74$

7. $(1.50 \text{ g HC}_7\text{H}_5\text{O}_2) \left(\frac{1 \text{ mol HBz}}{122.12 \text{ g}} \right) = 0.01228 \text{ mol HBz}$

$(1.50 \text{ g NaC}_7\text{H}_5\text{O}_2) \left(\frac{1 \text{ mol NaBz}}{144.1 \text{ g}} \right) = 0.01041 \text{ mol NaBz}$

a) buffer. mole ratio = molarity ratio.

$$K_a = \frac{[\text{H}^+][\text{Bz}^-]}{[\text{HBz}]} \quad [\text{H}^+] = K_a \left(\frac{\text{moles HBz}}{\text{moles Bz}^-} \right)$$

$$[\text{H}^+] = 6.3 \times 10^{-5} \left(\frac{0.01228 \text{ mol HBz}}{0.01041 \text{ mol NaBz}} \right) = 7.43 \times 10^{-5} \text{ M H}^+$$

$\text{pH} = 4.13$

b) to change the buffer pH to 4.00: need to add more of the weak acid. (pH is getting lower: more acidic).

Find the new ratio of A^-/HA that corresponds to this desired pH.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \xrightarrow{\text{desired.}} \quad \frac{K_a}{[\text{H}^+]} = \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\frac{6.3 \times 10^{-5}}{1.0 \times 10^{-4}} = \frac{0.63 \text{ A}^-}{1 \text{ HA}}$$

have to get this ratio by adding HBz to what we already have.

$$\frac{0.63 \text{ A}^-}{1 \text{ HA}} = \frac{0.01041 \text{ mol Bz}^-}{(0.01228 + x) \text{ mol HBz}}$$

7b continued

p.8

$$0.63(0.01228 + x) = 0.01041$$

$$0.007736 + 0.63x = 0.01041$$

$$0.63x = 0.00267$$

$$x = 0.00424 \text{ mol HBz!}$$

add this amount.

$$(0.00424 \text{ mol HBz}) \left(\frac{122.12 \text{ g HBz}}{1 \text{ mol HBz}} \right) =$$

add
0.52 g
benzoic
acid

check: new # mol HBz =

$$0.00424 \text{ mol} + 0.01228 \text{ mol} = 0.01652 \text{ mol HBz}$$

$$\text{find mole ratio: } \frac{0.01041 \text{ mol Bz}^-}{0.01652 \text{ mol HBz}} = 0.63!$$

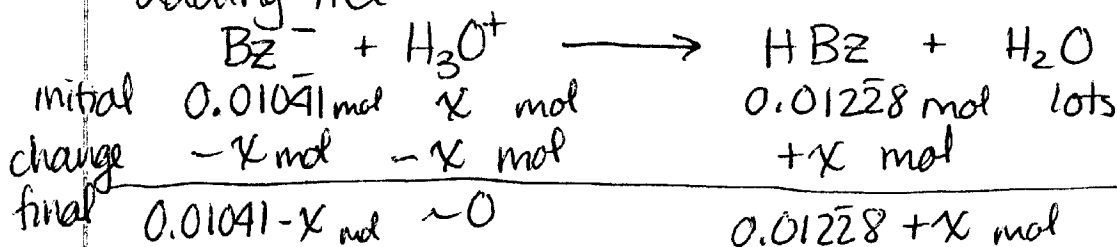
yes - it's the
same ratio
as before --

c) original buffer pH = 4.13.

want a buffer pH = 4.00. need to add HCl
to lower the pH.

in new buffer $\frac{K_a}{[H^+]} = \frac{[A^-]}{[HA]} = \frac{6.3 \times 10^{-5}}{1.0 \times 10^{-4}} = 0.63$
as in part B.

adding HCl:



$$\frac{[A^-]}{[HA]} = 0.63 = \frac{(0.01041 - x) \text{ mol Bz}^-}{(0.01228 + x) \text{ mol HBz}}$$

$$0.63(0.01228 + x) = (0.01041 - x)$$

$$0.007736 + 0.63x = 0.01041 - x$$

$$1.63x = 0.00267$$

$$x = 0.00164$$

x = # mol HCl
to add

7c continued

P. 9

$$(0.00164 \text{ mol HCl}) \left(\frac{L}{2.00 \text{ mol HCl}} \right) = 0.00082 \text{ L} \\ = 0.82 \text{ mL of } 2.00 \text{ M HCl!}$$

8. Want a buffer, pH = 12.10.
look @ the three K_a 's for H_3PO_4 .

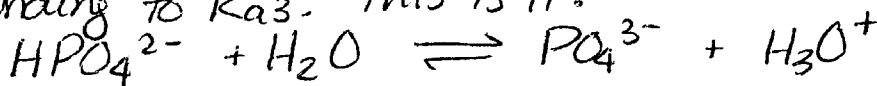
$pK_{a1} = 2.16$

$pK_{a2} = 7.21$

$pK_{a3} = 12.32$

this one is very close to 12.10.

So... use the equilibrium corresponding to K_{a3} . This is it:



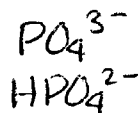
The pH is set at 12.10. Corresponds to $[H^+] = 7.94 \times 10^{-13} \text{ M}$

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$\frac{K_a}{[H_3O^+]} = \frac{[PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$\frac{4.8 \times 10^{-13}}{7.94 \times 10^{-13}}$$

$$= \frac{0.6045}{1}$$



this is the ratio in the buffer.

- 3 ways to make it:
- ① Mix HPO_4^{2-} and PO_4^{3-}
 - ② Add NaOH to HPO_4^{2-}
 - ③ Add HCl to PO_4^{3-} .

Looking at the ratio: the least concentrated buffer component is PO_4^{3-} . this is 0.10 M in the buffer.

$$\frac{0.6045}{1} \frac{PO_4^{3-}}{HPO_4^{2-}} = \frac{0.10 \text{ M}}{x \text{ M}} \frac{PO_4^{3-}}{HPO_4^{2-}}$$

$$0.10 = 0.6045 x$$

$$x = 0.1654 \text{ M } HPO_4^{2-} \text{ in the buffer.}$$

8. continued

p. 10

V_{tot} of buffer is 200 mL.

find moles of each in buffer.

$$(0.200 \text{ L}) \left(\frac{0.10 \text{ mol PO}_4^{3-}}{\text{L}} \right) = 0.020 \text{ mol PO}_4^{3-} \text{ in buffer.}$$

$$(0.200 \text{ L}) \left(\frac{0.1654 \text{ mol HPO}_4^{2-}}{\text{L}} \right) = 0.033 \text{ mol HPO}_4^{2-} \text{ in buffer.}$$

(in 200 mL.)

① Way 1: Mix the conj. acid and conj base.

need 0.020 mol PO_4^{3-} , 0.033 mol HPO_4^{2-} in 200 mL.

$$(0.020 \text{ mol PO}_4^{3-}) \left(\frac{1 \text{ mol Na}_3\text{PO}_4}{1 \text{ mol PO}_4^{3-}} \right) \left(\frac{163.94 \text{ g Na}_3\text{PO}_4}{1 \text{ mol Na}_3\text{PO}_4} \right) = 3.28 \text{ g Na}_3\text{PO}_4$$

$$(0.033 \text{ mol HPO}_4^{2-}) \left(\frac{1 \text{ mol Na}_2\text{HPO}_4}{1 \text{ mol HPO}_4^{2-}} \right) \left(\frac{141.96 \text{ g Na}_2\text{HPO}_4}{1 \text{ mol Na}_2\text{HPO}_4} \right) = 4.68 \text{ g Na}_2\text{HPO}_4$$

① put 3.3 g Na_3PO_4 and 4.7 g Na_2HPO_4 in a flask. dilute to a total volume of 200. mL.
⇒ Buffer, pH 12.10.

② Add NaOH to HPO_4^{2-} : $\text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$
convert some HPO_4^{2-} to PO_4^{3-} until the ratio of $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ is 0.6045/1. (this will give a pH of 12.10)

Again: final concentrations in the buffer should be: 0.10 M PO_4^{3-} , 0.1654 M HPO_4^{2-}
moles: 0.020 mol PO_4^{3-} , 0.033 mol HPO_4^{2-}

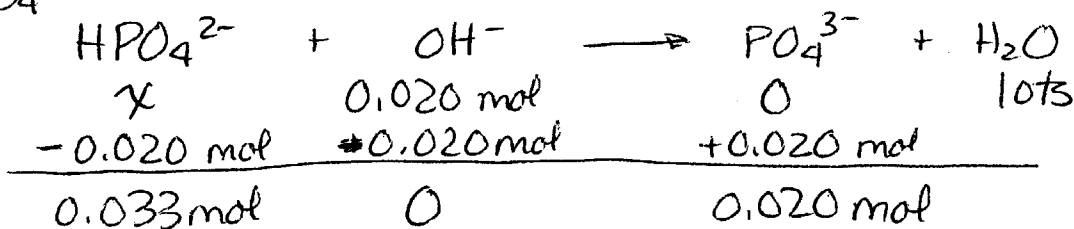


end: 0.033 mol ~0 0.020 mol

#8 continued

p. 11

So: Start with some HPO_4^{2-} .
add 0.020 mol OH^- ! (this will produce 0.020 mol PO_4^{3-} !)



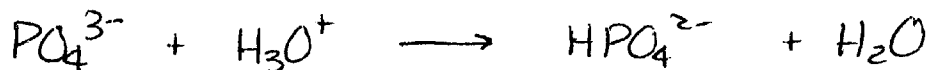
So $x - 0.020 \text{ mol} = 0.033 \text{ mol}$
 $x = 0.053 \text{ mol } \text{HPO}_4^{2-}$ initially.
 add 0.020 mol OH^- to it.

$$(0.053 \text{ mol } \text{Na}_2\text{HPO}_4) \left(\frac{141.96 \text{ g } \text{Na}_2\text{HPO}_4}{1 \text{ mol } \text{Na}_2\text{HPO}_4} \right) = 7.52 \text{ g } \text{Na}_2\text{HPO}_4$$

$$(0.020 \text{ mol } \text{NaOH}) \left(\frac{\text{L}}{1.00 \text{ mol } \text{NaOH}} \right) = 0.020 \text{ L} = 20. \text{ mL}$$

(2) So: put 7.5 g Na_2HPO_4 + 20. mL 1.00M NaOH into a flask. dilute to 200 mL with water.

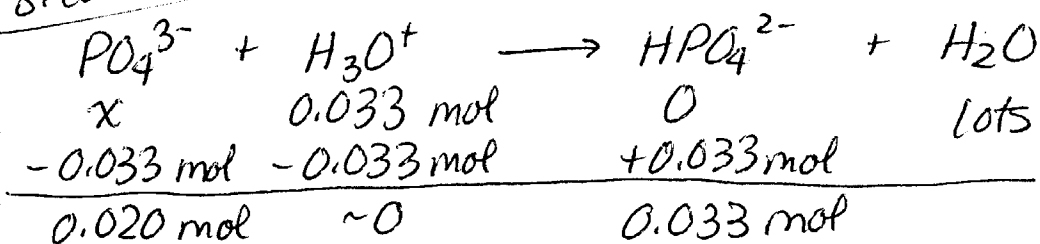
(3) Add HCl to PO_4^{3-} : $\text{PO}_4^{3-} + \text{H}_3\text{O}^+ \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$
 convert some PO_4^{3-} to HPO_4^{2-} until the ratio is 0.6045 $\text{PO}_4^{3-}/1 \text{ HPO}_4^{2-}$. (gives pH = 12.10).



end. 0.020 mol 0.033 mol ← as before

need to add H_3O^+ : 0.033 moles of it (because that will produce 0.033 mol HPO_4^{2-} .)

8. continued



$$x - 0.033 \text{ mol} = 0.020 \text{ mol}$$

$$x = 0.053 \text{ mol PO}_4^{3-} \text{ to start with.}$$

$$(0.053 \text{ mol Na}_3\text{PO}_4) \left(\frac{163.94 \text{ g Na}_3\text{PO}_4}{1 \text{ mol Na}_3\text{PO}_4} \right) = 8.69 \text{ g Na}_3\text{PO}_4$$

$$(0.033 \text{ mol HCl}) \left(\frac{1 \text{ L}}{1.00 \text{ mol HCl}} \right) = 0.033 \text{ L HCl} = 33 \text{ mL HCl}$$

(3) (50) add 8.7 g Na_3PO_4 and 33 mL of 1.00 M HCl to flask. dilute to a total of 200 mL with deionized water!