Buffers Made Easy Solutions

FIRST EXERCISE

K 18.5   a) 3.89   b) 3.86

a) Before: $K_a = 1.8 \times 10^{-4}$

$$[H^+] = K_a \frac{[A]}{[B]} = 1.8 \times 10^{-4} \frac{[.50]}{[.70]} = 1.286 \times 10^{-4}$$

$$\therefore pH = -\log[1.286 \times 10^{-4}] = 3.89$$

2 decimal places since 2 sig figs in M

b) After: I Added Acid! Respect [Molarity]

10 mL of 1.00M

$$[H^+] = 1.8 \times 10^{-4} \frac{[A^+]}{[B^-]} = 1.8 \times 10^{-4} \left[\frac{(.500 L \times .50M + .01L \times 1M)}{.510 L \text{ total volume}} \right]$$

Moles

$$\frac{.500 L \times .70M - .01L \times 1M}{.510 L \text{ total volume}}$$

Moles

$$= 1.8 \times 10^{-4} \frac{(.26 \text{ moles})}{(.34 \text{ moles})} = 1.38 \times 10^{-4}$$

$$\therefore pH = 3.86$$

Very little change

EXERCISE 2

Since we want a pH of 5   we know $[H^+] = 10^{-5}$
$K_a = 1.8 \times 10^{-5}$ ← which is good for a buffer w/ a pH of 5

$$[H^+] = K_a \frac{[A]}{[B]}$$

$10^{-5} = 1.8 \times 10^{-5} \text{ (Ratio)}$

$\frac{1 \times 10^{-5}}{1.8 \times 10^{-5}} = $ Ratio $= \underline{1 \text{ to } 1.8}$
                               ACID   BASE

Mix 1.0 mol ACID (HA) to 1.8 mol base (salt = NaA)
in enough water to dissolve the salt.
The amount of water is NOT critical, only the
relative amounts of A:B. You've noticed the "total
volume" part of the expression drops out.

EXERCISE 3a) What if you're given a K_b?! $K_a = \frac{K_w}{K_b}$

$K_b = 1.8 \times 10^{-5}$ 0.25M NH_3 with 0.40M NH_4Cl

$$[H^+] = K_a \frac{[A]}{[B]} = \frac{\overbrace{1 \times 10^{-14}}^{K_w}}{\underbrace{1.8 \times 10^{-5}}_{K_b}} \frac{[0.40 M]}{[0.25 M]} = 8.9 \times 10^{-10}$$

$\therefore pH = -\log[8.9 \times 10^{-10}] = 9.05$

EXERCISE 3b)

0.10 mole gaseous HCl added to 1L of soln' from a)

$$[H^+] = \boxed{\frac{K_w}{K_b}\frac{[A+]}{[B-]}} = \underset{Ka}{5.56\times10^{-10}} \frac{[\overset{moles!}{(0.40\,M \times 1.0\,L)} + .10\,mole]}{[\underset{moles!}{(0.25\,M \times 1.0\,L)} - .10\,mole]}$$

$$[H^+] = 5.56\times10^{-10}\frac{[.50]}{[.15]} = 1.85\times10^{-9}$$

$$\therefore pH = -\log 1.85\times10^{-9} = 8.73$$

Exercise 4 (typo- the problem in Zumdahl is 4.30)

a pH of 4.30 is desired $\therefore [H^+] = 10^{-4.30} = 5.011\times10^{-5}$

I need to select a Ka close to ⟶

Which makes both propanoic & benzoic good choices.

An ideal buffer has an A:B ratio of ⟨one⟩ so ...

$$[H^+] = 5.0\times10^{-5} = Ka\frac{[A]}{[B]}$$ Ratio Acid : Base

Chloroacetic $5\times10^{-5} = 1.35\times10^{-3}\left(\frac{A}{B}\right)$; $\left(\frac{A}{B}\right) = .037$

propanoic $5\times10^{-5} = 1.3\times10^{-5}\left(\frac{A}{B}\right)$; $\left(\frac{A}{B}\right) = 3.8$

* benzoic $5\times10^{-5} = 6.4\times10^{-5}\left(\frac{A}{B}\right)$; $\left(\frac{A}{B}\right) = .78$ * closest to 1.0 ∴ BEST choice!

hypochlorous $5\times10^{-5} = 3.5\times10^{-8}\left(\frac{A}{B}\right)$; $\left(\frac{A}{B}\right) = 1400$

FYI: pKa for benzoic is $-\log(Ka) = 4.19$ if ratio were 1:1 A:B
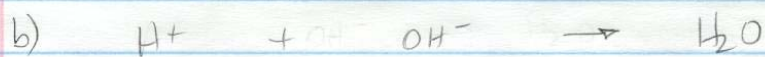
EXERCISE 5   The trick is to a) recognize as stoich. w/ LIMITING Reagent

b) track total * volume for molarity calculation

a) it's all about the pH of the acid

$$pH = -\log[.200] \quad \therefore \quad pH = 0.699 \quad (3\ sig.figs. = 3\ decimal\ places\ on\ pH)$$

b) H^+ + OH^- $\longrightarrow$ H_2O

initial   50ml × .2M   10ml × .1M

= 10^3 mmoles   = 1.0 mmoles

−1 mmole to neutralize   LIMITING!

after reaction $\therefore$ 9 mmoles left θ $\therefore [H^+] = \dfrac{9\ \text{mmoles}}{*60\ ml} = [.15]$

AND $pH = -\log[.15] = 0.824$

c) H^+ + OH^- $\longrightarrow$ H_2O

50ml × .2M   20ml × .1M

= 10^3 mmoles 8 mmoles left   = 2 mmoles $\to$ 0 LIMIT $\therefore [H^+] = \dfrac{8\ \text{mmoles}}{*70\ mL} = [.114]$

$pH = -\log[.114] = 0.942$

d) H^+ + OH^- $\longrightarrow$ H_2O

50ml × .2M   50ml × .1M

10 mmoles 5 mmoles remain   = 5 mmoles $\to$ 0 LIMIT $\therefore [H^+] = \dfrac{5\ \text{mmoles}}{*100\ ml} = [.050]$

$pH = -\log[.050] = 1.301$

e) H^+ + OH^- $\longrightarrow$ H_2O
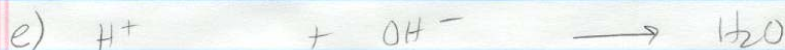
50ml × .2M   100ml × .1M

10 mmoles   =   10 mmoles $\longrightarrow$ all neutralized $\therefore$ Eq. pt.

$\therefore pH = 7.000$ since $\dfrac{moles}{strong\ acid} = \dfrac{moles}{strong\ base}$

EX5 cont

f)   H$^+$ +   OH$^-$ →   H$_2$O

50 mL X .2M   150 mL X .1M
10 m̶m̶i̶l̶e̶s̶ →0   1̶5̶ m̶m̶i̶l̶e̶s̶ → 5 m moles Excess   ∴ pOH = −log $\left[\dfrac{5\,m\,moles}{200\,mL}\right]$
     LIMIT
                                                    pOH = 1.602   ∴   pH = 12.398

g)   H$^+$ +   OH$^-$ →   H$_2$O
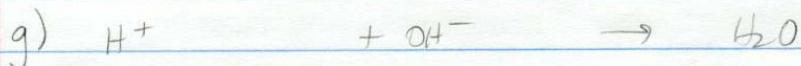
50 mL X .2M   200 mL X .1M
10 m̶m̶i̶l̶e̶s̶ →0   =̶2̶0̶ m̶m̶i̶l̶e̶s̶ → 10 excess   ∴ pOH = −log $\left[\dfrac{10\,m\,moles}{250\,mL}\right]$
     LIMIT
                                           pOH = 1.398   ∴   pH = 12.602

typo = 3 sf = 3 decimal places on pH

Exercise 6 K_a HCN = 6.2×10^{-10}

TRICK: Buffer to
eq. pt. → pH = pKa
@ ½ eq pt → at
eq. pt. hydrolyze salt !!
RICE

As soon as the NaOH mixes w/ HCN ==you have a buffer== of HCN + its salt Na^+CN^- . . .

a) $[H^+] = \boxed{K_a \dfrac{[A-]}{[B+]}} = 6.2 \times 10^{-10} \left(\dfrac{(50 \, m\ell \times .1M) - (8 \, m\ell \times .1M)}{58 \, m\ell} \middle/ \dfrac{0 + (8 \, m\ell \times .1M)}{58 \, m\ell} \right)$

$[H^+] = 6.2 \times 10^{-10} \left(\dfrac{5 \, mmoles - .8 \, mmoles}{.8 \, mmoles} \right) = 3.255 \times 10^{-9}$

$\therefore$ pH $= -\log(3.255 \times 10^{-9}) = $ ==8.487==

b) @ half way pt   ½ Acid → neutralized w/ base so
½ [BASE] Salt (NaCN) has also formed

$\underset{WK}{HCN} + \underset{STRONG}{NaOH} \rightarrow HCN + Na^+ + OH^- \xrightarrow{½ \, eqpt.} Na^+ + H_2O + \underbrace{CN^-}_{½} + \underbrace{HCN}_{½}$

==A perfect   A:B 1:1   buffer exists   and   pH = pKa==
==$\therefore$ pH $= -\log[6.2 \times 10^{-10}] = 9.208$==

c) all about the hydrolysis of the salt !! ₴ Stoichiometry!
@ eq. pt. moles HCN = moles NaOH = 5 mmoles SALT!! $\Rightarrow$ WKA vs. St. B ; pH > 7 Expect
   ⁕5 mmoles   =   5 mmoles   ⁕? = 50 mℓ ← that's why!
   (50 mℓ × .1M)   (? mℓ × .1M)

R $CN^- + H_2O \rightarrow HCN + OH^-$ ← just entered the
                                                "land of K_b"
I $\left[\dfrac{⁕5 \, mmoles}{100 \, m\ell} \right] = .05M$ 0   0
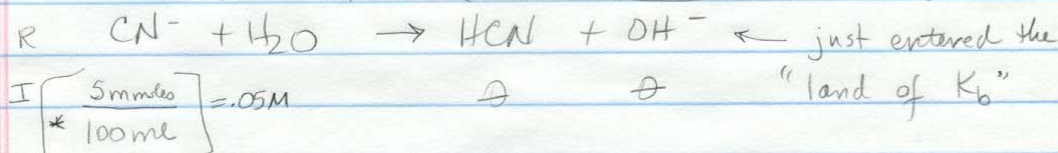
C $-x$ $+x$ $+x$
E $.05 - x$ x x

$K_b = \boxed{\dfrac{K_w}{K_a}} = \dfrac{1 \times 10^{-14}}{6.2 \times 10^{-10}} = \dfrac{x^2}{.05 - x}$ ← can neglect

$\therefore x = 8.98 \times 10^{-4} = [OH^-]$
pOH = 3.047 → ==pH = 10.953==

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Exercise 7

WK Base + Strong Acid ⟹ Expect acidic
eq. pt.

Look @ curve + data pg. 751
Eq. pt ≈ 5.36

Look at table a choose an indicator in
the 5-7 ish range

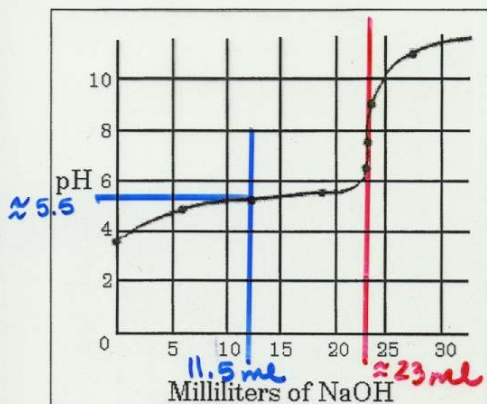==Methyl red is best choice==

Exercise 8

INDICATOR'S
Useful range = $pK_a \pm 1$

$K_a = 1.0 \times 10^{-7} = \dfrac{[H^+][In^-]}{[HIn]}$ Color change visible when $\dfrac{[In^-]}{[HIn]} = \dfrac{1}{10}$

$K_a = 1.0 \times 10^{-7} = \dfrac{[H^+][1]}{10}$

$[H^+] = 1 \times 10^{-6}$ or pH of 6.00 when the
color change is 1st visible

1988 D

A 30.00 millilitre sample of a weak monoprotic acid was titrated with a standardized solution of NaOH. A pH meter was used to measure the pH after each increment of NaOH was added, and the curve above was constructed.

(a) Explain how this curve could be used to determine the molarity of the acid.

The sharp vertical rise occurs @ eq. pt.
$\approx$ 23 ml NaOH added   AND

moles A = moles B ; 30ml (M_A) = 23ml (M_B)

$$M_A = \frac{23ml\,(M_B)}{30ml}$$

(b) Explain how this curve could be used to determine the dissociation constant K_a of the weak monoprotic acid.
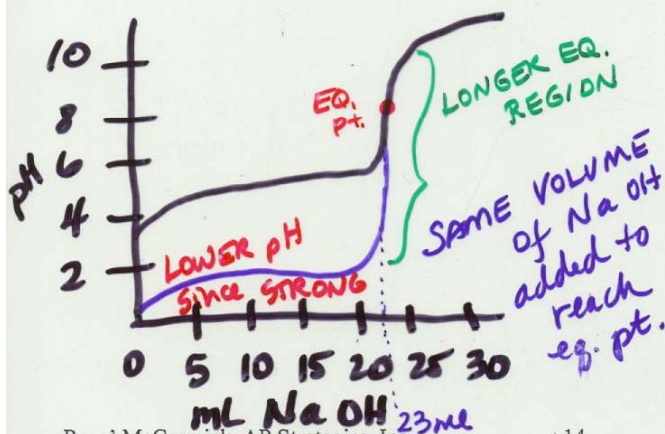
@ ½ eq. pt   pH = pKa

When $\frac{23}{2}$ = 11.5ml of base have been added, the pH $\approx$ 5.5 $\therefore$

$$10^{-5.5} = K_a = [H^+ \text{ also}]$$

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(c) If you were to repeat the titration using a indicator in the acid to signal the endpoint, which of the following indicators should you select? Give the reason for your choice.

Methyl red $K_a = 1 \times 10^{-5}$ pH $\approx$ 5   pKa = pH @ end pt.

Cresol red $K_a = 1 \times 10^{-8}$ 8
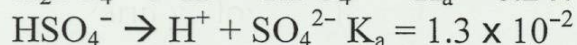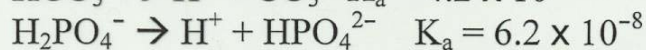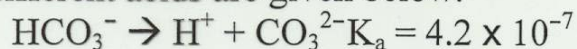
Alizarin yellow $K_a = 1 \times 10^{-11}$ 11

Looking at the graph, the end point occurs near 8 so cresol red is the best choice.

(d) Sketch the titration curve that would result if the weak monoprotic acid were replaced by a strong monoprotic acid, such as HCl of the same molarity. Identify differences between this titration curve and the curve shown above.

LONGER EQ. REGION

EQ. Pt.

LOWER pH SINCE STRONG

SAME VOLUME of Na OH added to reach eg. pt.

pH 10 8 6 4 2

0 5 10 15 20 25 30

mL Na OH 23mL

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1992 D *Essay* — No calculator! [NOW] had calc. in 1992

The equations and constants for the dissociation of three different acids are given below.

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$ $K_a = 4.2 \times 10^{-7}$

$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$ $K_a = 6.2 \times 10^{-8}$

$HSO_4^- \rightarrow H^+ + SO_4^{2-}$ $K_a = 1.3 \times 10^{-2}$

(a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Explain your choice.

pH of a buffer = pKa when ratio A:B is 1:1 ∴

$H_2PO_4^-$ & HPO_4^{2-} is the best choice w/ a Ka of

6.2×10^{-8} (pH = 7.2 = pKa)

(b) Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.

Dissolve equal # of moles of

$H_2PO_4^-$ & HPO_4^{2-} in water.

(c) If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.

pH would <u>NOT</u> be changed since the ratio of A:B would not change; $[H^+] = Ka \frac{[A]}{[B]}$

The capacity of the buffer would increase since there are more moles of A & B to react w/ added A or B.

(d) Explain briefly how you could prepare the buffer solution in (a) if you had available the solid salt of the only one member of the conjugate pair and solution of a strong acid and a strong base.

Add strong base to salt of conj. Acid <u>or</u>
Add strong acid to salt of conj. BASE

or, Use a pH meter & strong A or B to adjust to the desired pH.

1982 A $[H^+] = Ka \dfrac{[A]}{[B]}$

A buffer solution contains 0.40 mole of formic acid, HCOOH, and 0.60 mole of sodium formate, HCOONa, in 1.00 litre of solution. The ionization constant, K_a, of formic acid is 1.8×10^{-4}.

EASY

(a) Calculate the pH of this solution.

$$[H^+] = 1.8 \times 10^{-4} \dfrac{[.4]}{[.6]} = 1.2 \times 10^{-4}$$

$$\therefore pH = -\log 1.2 \times 10^{-4} = 3.92$$

Soln key has .6/.4 but correct answer ↑ (typo!)

(b) If 100. millilitres of this buffer solution is diluted to a volume of 1.00 litre with pure water, the pH does not change. Discuss why the pH remains constant on dilution.

$$[H^+] = Ka \dfrac{[A]}{[B]} \quad ; \quad \text{If the } \dfrac{A}{B} \text{ ratio does}$$

NOT change then $[H^+]$ does NOT change

and pH does NOT change!

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$.4M \times .1L = $ moles A

$.6M \times .6L = $ moles B

(b) A 5.00 millilitre sample of 1.00 molar HCl is added to 100. millilitres of the original buffer solution. Calculate the $[H_3O^+]$ of the resulting solution. $.005L \times 1M = .005$ moles

$$[H^+] = 1.8 \times 10^{-4} \left(\frac{.04 \, mol + .005 \, moles}{.06 \, mol - .005 \, moles} \right)$$

$$\boxed{[H^+] = 1.47 \times 10^{-4} M}$$

(d) A 800.0 milliliter sample of 2.00 molar formic acid is mixed with 200. milliliters of 4.80 molar NaOH. Calculate the $[H_3O^+]$ of the resulting solution.

$.800 L \times 2M = 1.60$ moles **WK ACID**

$.200 L \times 4.8M = -.96$ moles **STRONG BASE** } mix

$.64 mol$ **EXCESS ACID**

$$[H^+] = K_a \frac{[A^-]}{[B^+]}$$

$$[H^+] = 1.8 \times 10^{-4} \frac{[1.60 \, mol - .96 \, mol]}{0 + .96 \, mol}$$

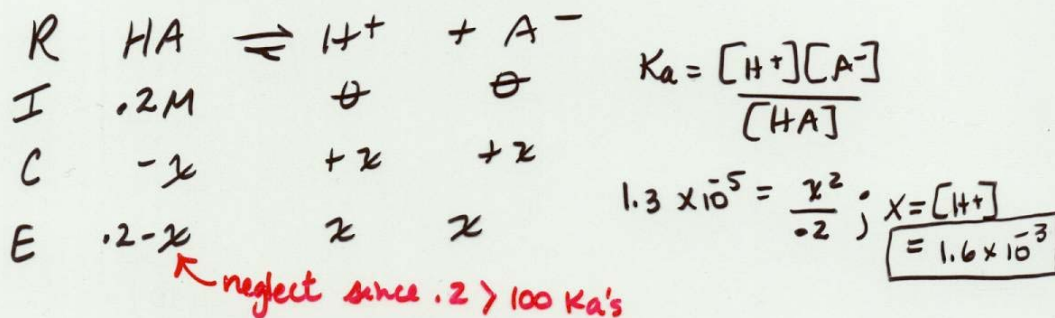$$= 1.8 \times 10^{-4} \frac{[.64]}{[.96]} = \boxed{1.2 \times 10^{-4}}$$

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1991 A

The acid ionization constant, K_a, for propanoic acid, C_2H_5COOH, is 1.3×10^{-5}.

   (a) Calculate the hydrogen ion concentration, $[H^+]$, in a 0.20 molar solution of propanoic acid.

R $HA \rightleftharpoons H^+ + A^-$ $K_a = \dfrac{[H^+][A^-]}{[HA]}$

I   .2M 0 0

C $-x$ $+x$ $+x$ $1.3 \times 10^{-5} = \dfrac{x^2}{.2}$; $x = [H^+]$

E $.2 - x$ x x $\boxed{= 1.6 \times 10^{-3}}$

↖ neglect since .2 > 100 Ka's

   (b) Calculate the percentage of propanoic acid molecules that are ionized in the solution in (a).

$$\dfrac{1.6 \times 10^{-3}}{.2} \times 100 = 0.81\% \text{ ionized}$$

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(b) What is the ratio of the concentration of propanoate ion, **BASE**
C$_2$H$_5$COO$^-$, ~~to~~ that of propan**ACID**oic acid in a buffer solution
with a pH of 5.20?

$$[H^+] = K_a \left(\frac{A}{B}\right) \text{ so } 10^{-5.20} = 1.3 \times 10^{-5}\left(\frac{A}{B}\right)$$

$$\left(\frac{A}{B}\right) = .485 \quad \text{MEAN!} \Rightarrow \frac{B}{A} = \frac{1}{.485} = \boxed{\begin{array}{c} 2.1 : 1 \\ \text{BASE : Acid} \end{array}}$$

(d) In a 100. milliliter sample of a different buffer solution, the
propanoic acid concentration is 0.35 molar and the sodium
propanoate concentration is 0.50 molar. To this buffer
solution, 0.0040 mole of <u>solid NaOH is added</u>. Calculate the
pH of the resulting solution.

$$[H^+] = K_a \frac{[A-]}{[B+]}$$

$$= 1.3 \times 10^{-5}\left(\frac{[(.35M \times .1L) - .004mol]}{[(.50M \times .1L) + .004mol]}\right)$$

$$[H^+] = 1.3 \times 10^{-5}\left(\frac{[.031]}{[.054]}\right) = 7.46 \times 10^{-6} \; ; \; \boxed{pH = 5.13}$$

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1993 A

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Methylamine, CH_3NH_2, is a weak base that reacts according to the equation above. The value of the ionization constant, K_b, is 5.25×10^{-4}. Methylamine forms salts such as methylammonium nitrate, $(CH_3NH_3^+)(NO_3^-)$.

(a) Calculate the hydroxide ion concentration, $[OH^-]$, of a 0.225 molar aqueous solution of methylamine.

$$K_b = \frac{x^2}{(.225 - x)} \text{ neglect} \quad ; \quad 5.25 \times 10^{-4} \times .225 = x^2$$

$$x = [OH^-] = .01087 = \boxed{1.09 \times 10^{-2}}$$

got carried away! $\left\{ \quad \therefore pOH = 1.96 \quad \& \quad pH = 12.04 \right.$

(b) Calculate the pH of a solution made by adding 0.0100 mole of solid methylammonium nitrate to 120.0 milliliters of a 0.225 molar solution of methylamine. Assume no volume change occurs.

BASE

$$[H^+] = K_a \frac{[A]}{[B]} = \left(\frac{1 \times 10^{-14}}{5.25 \times 10^{-4}}\right) \frac{\left[\frac{.01 \, mol}{.120 \, L}\right]}{[.225]} = 7.05 \times 10^{-12}$$

$$\therefore -\log(7.05 \times 10^{-12}) = pH = 11.15$$

(c) How many <u>moles</u> of either NaOH or HCl (state clearly which you choose) should be added to the solution in (b) to produce a solution that has a pH of 11.00? Assume that no volume change occurs.

Must lower pH ∴ Add ACID (HCl)

$$[H^+] = K_a \frac{[A+]}{[B-]}$$

$$1 \times 10^{-11} = \left(\frac{1 \times 10^{-14}}{5.25 \times 10^{-4}}\right)\frac{[.0833 + x]}{[.225 - x]}$$

$$.525 = \frac{(.0833 + x)}{(.225 - x)}$$

.118 − .525x = .0833 + x
+.525x   +.525x

.118 − .0833 = 1.525x

$$\frac{.0348}{1.525} = x = \boxed{.0228}$$

∴ moles = M × V
= (.0228M)(.120L)

(d) A volume of 100. milliliters of distilled water is added to the solution in (c). How is the pH of the solution affected? Explain.

moles = $\boxed{2.74 \times 10^{-3}}$ HCl added

No change in pH since the ratio of A:B has <u>NOT</u> changed

$$[A+] = k_a \, (Ratio) \; \leftarrow \text{Stays same} \; \therefore \; [H+] \text{ stays the same!}$$