Deriving Buffer Equation from CH 9

But first, what is a buffer?

A buffer is a mixture of
- a weak acid and conjugate base
- a weak base and conjugate acid.

So (differ by one H^+):
- acetic acid ($HC_2H_3O_2$) and sodium acetate ($NaC_2H_3O_2$) are a buffer
- ammonium (NH_4^+) and ammonia (NH_3) are a buffer

strong acid → hydrochloric acid (HCl) and chloride (Cl^-) are not!!

differ by 2 H^+ → H_2CO_3 and $CO_3^=$ are not!!

So setting up CHI?

$$HA \rightleftharpoons H^+ + A^-$$

HA	H^+	A^-
C_a	$\emptyset$	C_b
$-x$	$+x$	$+x$
$C_a - x$	x	$C_b + x$

note: HA, A^- are a buffer.

1. start with C_a of weak acid and C_b of conj. base
2. Assume H^+ from H_2O is negligible
3. identify equilibrium amounts in terms of x
4. substitute $x = H^+$ in K_a
5. Assume $[H^+]$ is small because we have weak acid + base
   $C_b + H^+ \to C_b$
   $C_a - H^+ \to C_a$
6. rearrange to buffer eqn.

$$K_a = \frac{(x)(C_b + x)}{(C_a - x)}$$

$$K_a = \frac{[H^+]([C_b + [H^+])}{(C_a - [H^+])}$$

$$K_a = \frac{[H^+]\,C_b}{C_a}$$

$$H^+ = K_a \frac{C_a}{C_b}$$

Wow, anyone can derive the buffer equation!!

Example. What is pH of a 0.1 M acetic acid and 0.1 M sodium acetate solution if $K_a = 1\times10^{-5}$.

note we have acetic acid : HA } conjugate acid

acetate : A^- } + base ≡ buffer

so use buffer equation

$$H^+ = K_a \frac{C_a}{C_b} = 1\times10^{-5}\left(\frac{0.1}{0.1}\right) = 1\times10^{-5}$$

pH = 5

note that $H^+ \approx K_a$ for a buffer.

Also note that for buffer equation to work, same conditions for C_a, C_b and K_a apply.

1. $C_a + C_b$ large
2. K_a in 10^{-4} to 10^{-10} range

Now for something completely different:

Neutralization.

What happens when I put an H^+ or an OH^- in solution? It looks to react.

H^+ looks for most basic thing in solution

$H^+ + OH^- \rightarrow H_2O$ lots of heat

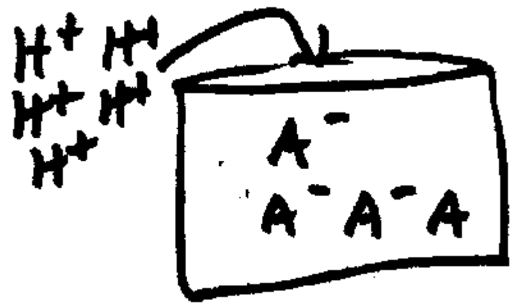
but if no OH^- then look for weak base

$H^+ + A^- \rightarrow HA$ a little heat

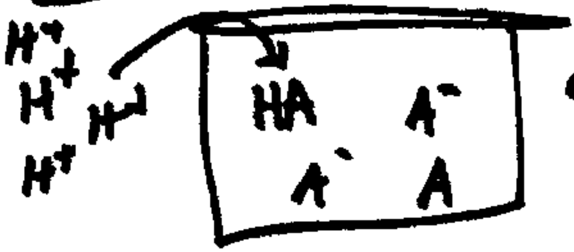
but if no A^- then H_2O

$H^+ + H_2O \rightarrow H_3O^+$ hydronium ion.

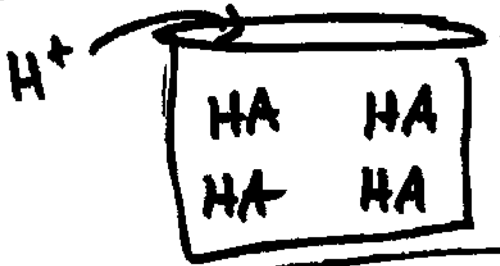
So follow the addition of 5 H^+ to 4 A^- in solution



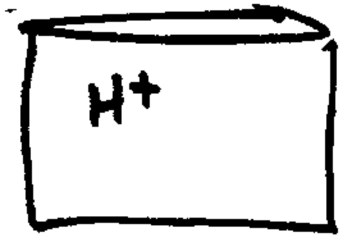
case 1 : $\emptyset$ H^+ added, only A^- in solution, weak base case, used $OH^- = (K_b C_b)^{1/2}$



case 2 : add 1 H^+. Now HA and A^- present. This is a buffer. use $H^+ = K_a \frac{C_a}{C_b}$



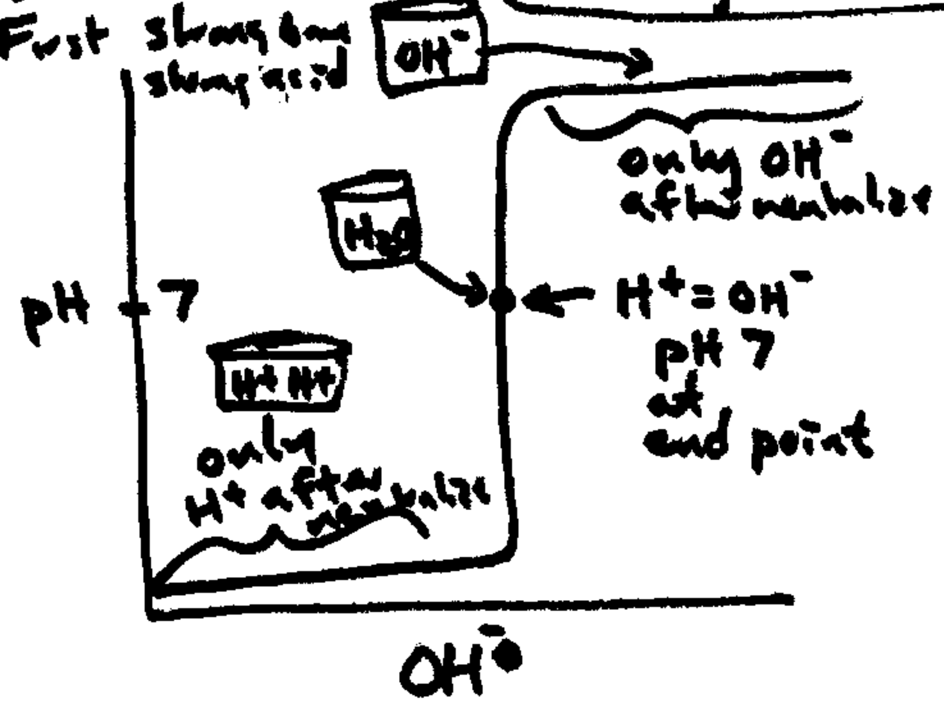
case 3 : add 4 H^+. Now only HA present. This is weak acid. use $H^+ = (K_a C_a)^{1/2}$



case 4 : add 5 H^+. Now have 1 H^+ and 4 HA. But HA makes little HA, so assume strong acid case $H^+ = C_a$

On to titration.

Two types: strong titrate strong
strong titrate weak



Here strong base titrates strong acid.
Note 3 regions
acid $pH = -\log[H^+] = C_a$
neutral $pH = pOH = 7$
base $pOH = -\log[H^+] = C_b$

Example calculation: what is the pH when I titrate 100 ml of 0.1M HCl with 50 ml of .2M NaOH?

moles $H^+ = (.1)(.1) = .01$ moles $OH^- = (.1)(.1) = .01$ $H^+ = OH^-$ so $pH = 7$

Example calculation: what is pH 50 ml .1M OH^- is added to 100 ml .1M H^+? moles $H^+ = (.1)(.1) = .01$ moles $pH = -\log\left[\frac{.005}{.150}\right]$

moles $OH^- = (.05)(.1) = .005$ after neutralize .005 moles H^+ $= 1.48$

Second case: weak titrated by strong. Difference is the neutralization

$A^- + H^+ \rightleftharpoons HA$ ⇐ HA is not water so end point isn't pH 7