More fun w/ buffers!

120.0 mL of our buffer → 1.50 M CH_3CO_2Na ; 1.00 M CH_3CO_2H (pH = 4.92)

+ add 10.0 mL of 2.00 M $HCl_{(aq)}$. (strong acid.)

pH = ?

$$HCl_{(aq)} \xrightarrow{100\%} H^+_{(aq)} + Cl^-_{(aq)}$$

(strong; Cl^- ↑ neutral (ignore))

strong ↓ ; from buffer ↓

$$H^+_{(aq)} + CH_3CO_2^-{}_{(aq)} \longrightarrow CH_3CO_2H_{(aq)}$$

Problem: Volumes change, then [ ] change

So... its easier to work w/ moles.

$$\#\,H^+ = 10.0\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{2.00\text{ mol HCl}}{1\text{ L}} \times \frac{1\text{ mol }H^+}{1\text{ mol HCl}} = 0.0200\text{ mol }H^+$$

$$CH_3CO_2^- : 120.0\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1.50\text{ mol }CH_3CO_2Na}{1\text{ L}} \times \frac{1\text{ mol }CH_3CO_2^-}{1\text{ mol }CH_3CO_2Na} = 0.180\text{ mol }CH_3CO_2^-$$

CH_3CO_2H ... 0.120 mol CH_3CO_2H

let's write out neut rxn!

$$H^+_{(aq)} \text{ (STRONG)} + CH_3CO_2^-{}_{(aq)} \longrightarrow CH_3CO_2H_{(aq)}$$

	H^+	$CH_3CO_2^-$	CH_3CO_2H
I	0.0200	0.180	0.120
C	−0.0200	−0.0200	+0.0200
E	0	0.160 (#mol)	0.140 → 1.08 M

$[CH_3CO_2^-] = \frac{0.160\text{ mol}}{0.130\text{ L}} = 1.23\text{ M}$ (0.130 L ↑ 120 mL buffer + 10 mL acid)

pH of sol^n? ICE Chart it! (Ka rxn)

$$CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO_2^-{}_{(aq)}$$

	CH_3CO_2H	H_2O	H_3O^+	$CH_3CO_2^-$
I	1.08 M	—	≈0	1.23 M
C	−x	—	+x	+x
E	(1.08 − x)	—	(x)	(1.23 + x)

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]_{eq}}$$

if $x \ll 1.08$

$$\Rightarrow 1.8\times10^{-5} = \frac{(x)(1.23+x)}{(1.08-x)} \approx \frac{(x)(1.23)}{(1.08)}$$

$$x = \frac{1.8\times10^{-5} \times 1.08}{1.23} = 1.6\times10^{-5}$$

5% rule ✓ $\Rightarrow [H^+] = 1.6\times10^{-5}$

$pH = -\log(x) = 4.80$

(decrease of 0.12 units of pH)

Preparing a Buffer w/ a specific pH

Buffer: Weak acid (HA) + conj. base (A^-)

K_a rxn: $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]_{eq}}.$$

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

$-\log_{10}[\ ]$

$$-\log_{10}[H_3O^+] = -\log\left(K_a \times \frac{[HA]}{[A^-]}\right)$$

$\log(A\cdot B) = \log A + \log B$

$$\Rightarrow pH = -\log_{10} K_a + -\log_{10}\frac{[HA]}{[A^-]}$$

$-1 \times \log\frac{[HA]}{[A^-]}$

$\log A^b = b\cdot\log A$

ex: $-\log A = \log A^{-1}$

ex: $-\log\frac{a}{b} = \log\left(\frac{a}{b}\right)^{-1} = \log(b/a)$

$$\Rightarrow pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Henderson–Hasselbalch equation

H–H eQ.

$$pH = pK_a + \log \frac{[base]}{[acid]}$$ ← conj.

"best" buffer is when $[base] \simeq [acid]$

$$\Rightarrow \quad \frac{[base]}{[acid]} = 1$$

$$pH = pK_a + \log 1$$ ($\log 1 \to 0$)

$$pH \simeq pK_a$$ best buffer

Caveat: ① Buffers are only 'good' if pH is within 1-unit of pKa.

H-H

② [base] and [acid] in our H-H eq^n refer to eq^m concs... we will often assume that these are same as orig conc from a dilution.

Ex: we want to make 1.0-L of a "phosphate" buffer w/ pH of 7.05

H_3PO_4 triprotic weak acid.

$K_{a1} = 7.5 \times 10^{-3}$

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

$K_{a2} = 6.2 \times 10^{-8}$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$K_{a3} = 4.8 \times 10^{-13}$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$