$y \simeq 2.000\,K_a$

FOR ACETIC ACID $K_a = 1.76 \times 10^{-5}$

$[H_3O^+] = 3.52 \times 10^{-5}\,M >> 10^{-7}\,M$

$pH = 4.453$

ADD 0.100 mol OF HCl.

ASSUMPTION: TAKE ALL OF THE H_3^+ FROM HCl AND COMBINE THEM WITH A^- TO FORM HA. NOW RECALCULATE THE pH.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

	HA(aq)	$H_2O(l)$	$H_3O^+(aq)$	$A^-(aq)$
I	1.100	—	$\simeq 0$	0.400
C	$-y$	—	y	$+y$
E	$1.100 - y$	—	y	$0.400 + y$

$$K_a = \frac{(0.400 + y)\,y}{(1.100 - y)} \simeq \frac{0.400 \cdot y}{1.100}$$

$$y \simeq \frac{1.100}{0.400} K_a = 4.84 \times 10^{-5}$$

$pH = 4.315$

IN NEUTRAL WATER, pH = 7.000, THE ADDITION OF 0.100 mol OF HCl TO ONE LITER WOULD HAVE CHANGE THE pH FROM 7 TO 1.

IN GENERAL

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

THUS

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

$$\simeq K_a \frac{[HA]_0}{[A^-]}$$

IF $K_a << 10^{-7}$, WHICH IMPLIES THAT THE CHANGE TO $[HA]_0$ AND $[A^-]_0$ IS NEGLIGIBLE.

$$pH = pK_a - \log_{10}\left(\frac{[HA]_0}{[A^-]_0}\right)$$

FOR A TARGET pH AND A SELECTED PAIR OF ACID / CONJ. BASE WITH K_a,

THE RATIO $\frac{[HA]_0}{[A^-]_0}$ IS DETERMINED

ALTHOUGH THE RATIO IS INDEPENDENT OF THE VALUE OF $[HA]_0$, SINCE WE CAN ADJUST $[A^-]$, THE LARGER VALUE OF $[HA]_0$ THE HIGHER BUFFER CAPACITY.

PREPARATION

ACID + CONJ. BASE SALT

CH_3COOH + $NaCH_3COO$

$\downarrow$ SOL $\qquad\qquad$ $\downarrow$ SOL

MOST CH_3COOH $\qquad\qquad$ CH_3COO^-

START SALT AND PROTONATE SOME OF THE ANION

$NaCN \rightarrow CN^- \xrightarrow{HCl} HCN$

TITRATION CURVES

STRONG ACID WITH A STRONG BASE

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

1.- V=0 (100.00 - 0.1000M HCl)

$pH = 1$ $\qquad n_{H^+} = 1.000\ 10^{-2}$ mol

2.- V = 30.00 mL OF BASE => 3.000×10^{-3} mol

=> $n_{H^+} = 7.000 \times 10^{-3}$ mol

$$[H_3O^+] = \frac{7.000 \times 10^{-3} \text{ mol}}{.1300 L} = 53.85 \times 10^{-3} M$$

$$= 5.385 \times 10^{-2} M$$

$pH = 1.2688 = \boxed{1.269}$

3.- $V = 99{,}95$ mL (100,00 mL - ONE DROP)

$n_{HO^-} = 9{,}995 \times 10^{-3}$ mol

$n_{H^+} = 5 \times 10^{-6}$ mol

$$[H_3O^+] = \frac{5 \times 10^{-6} \text{ mol}}{199{,}95 \text{ mL}} = 2.\underline{\underline{5}} \times 10^{-5} \text{ M}$$

pH = 4.7

4.- $V = 100.05$ mL (100,00 mL + ONE DROP)

100,00 mL OF BASE NUTRALIZE THE ACID.
THUS WE HAVE ONE DROP EXCESS OF BASE

$n_{OH^-} = 5, \times 10^{-2}$ mL $1{,}000 \times 10^{-1}$ M

$n_{OH^-} = 5 \times 10^{-6}$ mol

$$[OH^-] = \frac{5 \times 10^{-6} \text{ mol}}{200.05 \text{ mL}} = 2.\underline{\underline{5}} \times 10^{-5} \text{ M}$$

pOH = 4.7

pH = 9.3

WEAK ACID WITH STRONG BASE

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

0.1000	—	≈ 0	0
$-y$	—	$+y$	$+y$
$0.100 - y$		y	y

$$K_a = \frac{y^2}{0.1000 - y} \approx \frac{y^2}{0.1000}$$

$$y = \sqrt{0.1000\, K_a}$$

$$= \sqrt{1.000 \times 10^{-1}\ 1.76 \times 10^{-5}}$$

$$= \sqrt{1.76} \times 10^{-3} = 1.33 \times 10^{-3}$$

$$pH = 2.876$$

CONSIDER 100 mL OF 0.1000 M [HA]

AND USE NaOH SOLUTION OF 0.1000 M.

$\Rightarrow$ 1.000×10^{-2} mol OF ACID

moles of H_3^+O = 1.000×10^{-2} in 100 mL

ADD 30.00 mL OF NaOH SOL

# of moles of OH^- = 30.00×10^{-3} L 1.000×10^{-1} M
= 3.000×10^{-3}

ASSUME THAT OH^- REACT WITH HA

$n_{HA} = 7.000 \times 10^{-3}$

$n_{A^-} = 3.000 \times 10^{-3}$ ~~$+ 1.33 \times 10^{-4}$~~ $\simeq 3.000 \times 10^{-3}$

$n_{H^+} = 1.33 \times 10^{-4}$

$V_t = 0.130$ L

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

5.38×10^{-2}	1.02×10^{-3}	2.31×10^{-2}
$+y$	$-y$	$-y$
$5.38 \times 10^{-2} + y$	$1.02 \times 10^{-3} - y$	$2.31 \times 10^{-2} - y$

$$K_a = \frac{(1.02\times10^{-3} - y)(2.31\times10^{-2} + y)}{(5.38\times10^{-2} + y)}$$

$$10^{3} K_a = \frac{(1.02 - x)(23.1 - x)}{(53.8 + x)}$$

$$\bar{K}\,53.8 + \bar{K}x = (1.02)(23.1) + x^2 - 24.12x$$

$$x^2 - [24.12 + \cancel{\bar{K}}]x + (1.02)(23.1) - \cancel{53.8\bar{K}} = 0$$

$$x^2 - 24.12x + 23.6 = 0$$

$$x = \frac{+24.12 \pm \sqrt{(24.12)^2 - 4(23.6)}}{2}$$

$$x = \frac{24.12 - \sqrt{(24.12)^2 - 4(23.6)}}{2}$$

$$x = \frac{24.12 - 22.08}{2} = \frac{2.04}{2} = 1.02\,!$$

$$K_a \simeq [H_3O^+]\ \frac{2.31\times10^{-2}}{5.38\times10^{-2}}$$

$$[H_3O^+] = K_a \frac{5.38}{2.31}$$

$$pH = pK_a - \ln\left(\frac{5.38}{2.31}\right)$$

$$pH = 4.75 - 0.37 = 4.38$$

AT THE EQUIVALENCE POINT

$n_{OH^-} = 1.000 \times 10^{-2}$

ASSUME THAT ALL OH^- REACTS

SUCH THAT ALL $HA \longrightarrow A^-$

$$HA + OH^- \longrightarrow A^- + H_2O$$

THEFORE $n_{HA} = 0$ $V_T = 0.200$ L

$n_{A^-} = 1.000 \times 10^{-2}$

$$A^- + H_2O \rightleftharpoons HA + OH^- \quad \frac{K_w}{K_a}$$

	A^-	H_2O	HA	OH^-
I	5×10^{-2}	—	0	≈ 0
C	$-y$	—	y	y
E	$5 \times 10^{-2} - y$	—	y	y

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_a$$

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \quad \frac{1}{K_w}$$

$$HA + OH^- \rightleftharpoons A^- + H_2O \quad \frac{K_a}{K_w}$$

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_b$$

$$K_w = K_a K_b$$

BUT IN THE EXCESS OF OH^-

$$HA + OH^- \longrightarrow A^- + H_2O \qquad \frac{K_a}{K_w}$$

~~A~~T THE EQUIVALENCE POINT

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

	A^-	H_2O	HA	OH^-
I	5×10^{-2}	—	0	$\simeq 0$
C	$-y$	—	y	y
E	$.05 - y$	—	y	y

$$K_b = \frac{y^2}{0.05 - y} \simeq \frac{y^2}{0.05} = \frac{1.00 \times 10^{-14}}{1.76 \times 10^{-5}}$$

$$y = \sqrt{0.05\, K_b}$$

$$= \sqrt{5 \times 10^{-2} \cdot 5.68 \times 10^{-10}}$$

$$= 5.32 \times 10^{-6}$$

$$pOH = 5.3$$

$$pH = 8.7$$

POLYPROTIC ACIDS

MULTIPLE EQUILIBRIA

CO_3^{2-} / HCO_3^-
HCO_3^- / H_2CO_2

} WITH THE SAME $[H_3O^+]$

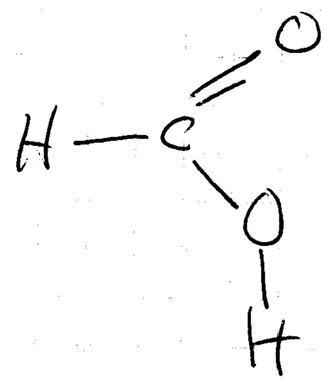
CONSERVATION OF MASS

$$[H_2CO_3] + [HCO_3^-] + [CO_3^-] = [C]_0$$

3 UNKNOWNS AND 3 EQ. !

CONDITIONS FAVORS ON SPECIES. !

NETTLE → FORMIC ACID



DOCK LEAF → SAP

↓

NATURAL AMINES

(UREA)

SAP is ALKALINE