Polyprotic Acid-Base Equilibria (Chapter 9)

Polyprotic - donate or accept more than one H^+
e.g., H_3PO_4 – can donate 3 H^+ ; triprotic acid.
H_2CO_3 – can donate 2 H^+; diprotic acid.

Diprotic acid (H_2A) (Sec. 9-1)

Stepwise hydrolysis:

$H_2A \rightleftharpoons H^+ + HA^-$ $K_{a1} = [H^+][HA^-]/[H_2A]$ $HA^- + H_2O \rightleftharpoons H_2A + OH^-$ $K_{b2} = [H_2A][OH^-]/[HA^-]$
$HA^- \rightleftharpoons H^+ + A^{2-}$ $K_{a2} = [H^+][A^{2-}]/[HA^-]$ $A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$ $K_{b1} = [HA^-][OH^-]/[A^{2-}]$

Case 1: solution of H_2A
Case 2: mixture of H_2A and HA^- (Sec. 9-2)
Case 3: solution of HA^-
Case 4: mixture of HA^- and A^{2-} (Sec. 9-2)
Case 5: solution of A^{2-}

Case 1: Fully protonated form: e.g., a diprotic acid H_2A

Example: Calc. pH of a 0.0100 M solution of carbonic acid. (H_2CO_3)
$K_{a1} = 4.45\times10^{-7}$ and $K_{a2} = 4.69\times10^{-11}$

	H_2CO_3	$\rightleftharpoons$	H^+	+	HCO_3^-
Initial:	0.01 M		0		0
Change	-X		+X		+X
Equil:	0.01-X		X		X

$K_{a1} = [H^+][HCO_3^-]/[H_2CO_3] = X^2/(0.01M-X) = 4.45\times10^{-7}$
$X^2/0.01M = 4.45\times10^{-7}$
$X = 6.67\times10^{-5}$ M = $[H^+]$
pH = 4.176

	HCO_3^-	$\rightleftharpoons$	H^+	+	CO_3^{2-}
Monoprotic calc	6.67×10^{-5}M		6.67×10^{-5}M		?

$K_{a2} = \cancel{[H^+]}[CO_3^{2-}]/\cancel{[HCO_3^-]}$
$K_{a2} \approx [CO_3^{2-}]$

Case 2: A mixture containing H_2A and HA^-

- If $K_{a1}/K_{a2} \geq 100$, the 2nd hydrolysis rxn can be neglected
- weak acid in the presence of its conjugated base = buffer

Example: Calc pH of a solution containing 0.100 M o-phthalic acid and 0.250 M potassium hydrogen o-phthalate. For $C_6H_4(COOH)_2$, $K_{a1} = 1.12\times10^{-3}$ and $K_{a2} = 3.91\times10^{-6}$

$K_{a1} / K_{a2} = 1.12\times10^{-3} / 3.91\times10^{-6} = 286 > 100$
- can neglect the 2nd hydrolysis rxn.

$pH = pK_a + \log C_{HA-} / C_{H2A} = -\log(1.12\times10^{-3}) + \log(0.250M/0.100M)$
$= 3.349$

Case 3: Solution HA^-

- HA^- is *amphiprotic* (accept and donate H^+)

$HA^- \rightleftharpoons A^{2-} + H^+$ $K_{a2} = [H^+][A^{2-}]/[HA^-]$

$HA^- + H_2O \rightleftharpoons H_2A + OH^-$ $K_{b2} = [H_2A][OH^-]/[HA^-]$

- The two equilibria occur simultaneously and both must be considered in deriving an equation for calculating $[H^+]$:

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HA^-] + K_wK_{a1}}{K_{a1} + [HA^-]}}$$

Example: Calc. pH of a 0.0250 M solution of sodium bicarbonate $NaHCO_3$. For H_2CO_3, $K_{a1} = 4.45\times10^{-7}$ and $K_{a2} = 4.69\times10^{-11}$

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HA^-] + K_wK_{a1}}{K_{a1} + [HA^-]}}$$

$$[H^+] = \sqrt{\frac{(4.5x10^{-7})(4.69x10^{-11})0.0250M + (1.0x10^{-14})(4.5x10^{-7})}{(4.5x10^{-7}) + 0.0250M}}$$

$[H^+] = 4.5_9 \text{ x } 10^{-9}$ M

$pH = 8.33_8$

If $K_{a2}F >> K_w$ and $K_{a1} << F$, then $[H^+] \cong \sqrt{K_{a1}K_{a2}} = 4.5_9 \text{ x } 10^{-9}$ M

Case 4: A mixture containing HA^- and A^{2-}

- If $K_{b1}/K_{b2} \geq 100$, the 2nd hydrolysis (K_{b2}) can be neglected
- thus final solution consists of HA^- and A^{2-} = buffer

Example: Calc. pH of a mixture of 0.10 M $NaHCO_3$ and 0.20 M Na_2CO_3.
For H_2CO_3, $K_{a1} = 4.45\times10^{-7}$ and $K_{a2} = 4.69\times10^{-11}$

Mixture of HCO_3^- and CO_3^{2-}, so buffer based on K_{a2}
$pH = pK_{a2} + \log C_{CO32-} / C_{HCO3-}$
$= -\log (4.69\times10^{-11}) + \log 0.20M/0.10M$
$= 10.65$

Case 5: A solution containing A^{2-}

- If $K_{b1}/K_{b2} \geq 100$, the 2nd hydrolysis rxn (K_{b2}) can be neglected.
- only the 1st hydrolysis rxn needs to be considered in pH calc.

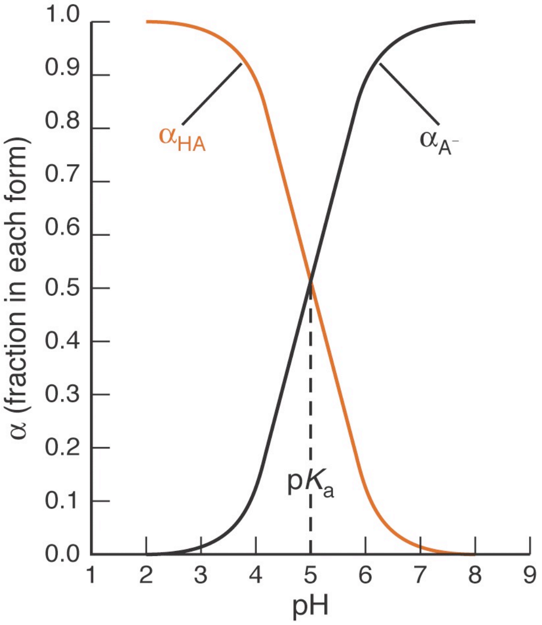
Example: Calc pH of a 0.150 M sodium oxalate solution ($Na_2C_2O_4$). For $H_2C_2O_4$,
$K_{a1} = 5.60\times10^{-2}$ and $K_{a2} = 5.42\times10^{-5}$

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$$

	$C_2O_4^{2-}$ + H_2O	⇌ $HC_2O_4^-$	+ OH^-
Initial:	0.150 M	0	0
Change	-x	+x	+x
Equil:	0.150 –x	x	x

$K_{b1} = K_w / K_{a2} = 1.0\times10^{-14} / 5.42\times10^{-5} = 1.85\times10^{-10}$
$K_{b1} = x \bullet x/(0.150M – X) = 1.85\times10^{-10}$
$x^2/0.150 = 1.85\times10^{-10}$ or $x = 5.27\times10^{-6}$ M = $[OH^-]$
pOH = 5.278
pH = 14 – pOH = 14 – 5.278 = 8.722

Fractional Composition (α) – fraction of specific form of a molecule relative to all forms of a molecule



For monoprotic acids:

$$\alpha_{A-} = \frac{[A^-]}{F_{acid}} = \frac{[A^-]}{[HA]+[A^-]} = \frac{K_a}{[H^+]+K_a}$$

$$\alpha_{HA} = \frac{[H^+]}{[H^+]+K_a}$$

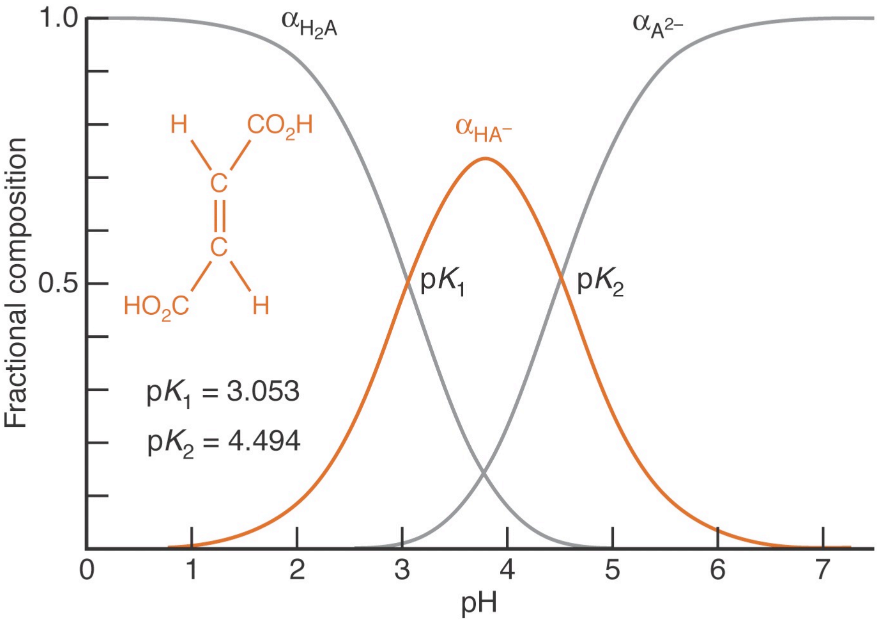
For diprotic acids:

$$\alpha_{\mathrm{H_2A}} = \frac{[\mathrm{H_2A}]}{\mathrm{F}} = \frac{[\mathrm{H^+}]^2}{[\mathrm{H^+}]^2 + \mathrm{K_{a1}}[\mathrm{H^+}] + \mathrm{K_{a1}K_{a2}}}$$

$$\alpha_{HA-} = \frac{[HA^-]}{F} = \frac{\mathrm{K_{a1}}[\mathrm{H^+}]}{[\mathrm{H^+}]^2 + \mathrm{K_{a1}}[\mathrm{H^+}] + \mathrm{K_{a1}K_{a2}}}$$

$$\alpha_{\mathrm{A^{2-}}} = \frac{[\mathrm{A^{2-}}]}{\mathrm{F}} = \frac{\mathrm{K_{a1}K_{a2}}}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]\mathrm{K_{a1}} + \mathrm{K_{a1}K_{a2}}}$$

Fumaric acid (Fig. 9-4)



Example #1: For the diprotic acid, fumaric acid (H_2A), pK_{a1} = 3,053, pK_{a2} = 4.494, what is the pH of a 0.050 M solution of HA^-. What is the pH? How much of each protic species is present?

$$\left[H^+\right]=\sqrt{\frac{K_{a1}K_{a2}[HA^-]+K_wK_{a1}}{K_{a1}+[HA^-]}}$$

$$\left[H^+\right]=\sqrt{\frac{10^{-3.053}10^{-4.494}(0.050M)+1.0x10^{-14}10^{-3.053}}{10^{-3.053}+0.050M}} = 1.67x10^{-4}\ M$$

pH = 3.78

$$\alpha_{H_2A}=\frac{[H^+]^2}{[H^+]^2+K_{a1}[H^+]+K_{a1}K_{a2}}$$

$$=\frac{(1.67x10^{-4})^2}{(1.67x10^{-4})^2+10^{-3.053}(1.67x10^{-4})+10^{-3.053}10^{-4.494}}$$

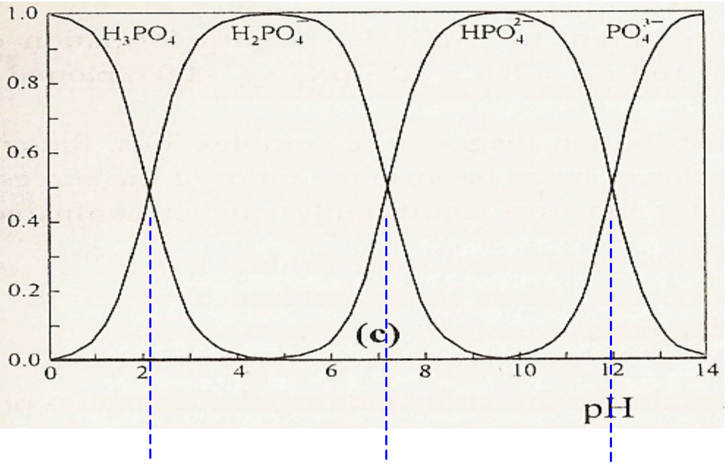
$$=\frac{2.79x10^{-8}}{2.79x10^{-8}+1.48x10^{-7}+2.83x10^{-8}}$$

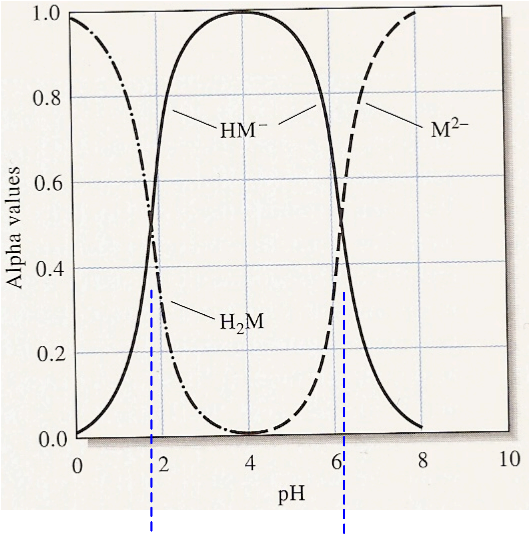
$$=\frac{2.79x10^{-8}}{2.04x10^{-7}}=0.137$$

$$\alpha_{HA-}=\frac{K_{a1}[H^+]}{[H^+]^2+K_{a1}[H^+]+K_{a1}K_{a2}}=\frac{1.48x10^{-7}}{2.04x10^{-7}}=0.724$$

$$\alpha_{A^{2-}}=\frac{K_{a1}K_{a2}}{[H^+]^2+[H^+]K_{a1}+K_{a1}K_{a2}}=\frac{2.84x10^{-8}}{2.04x10^{-7}}=0.139$$

Triprotic Acids (H_3A)

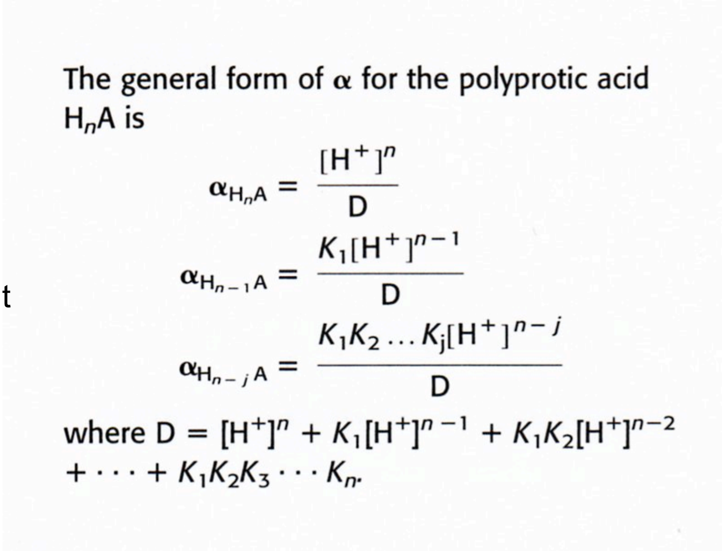




pK_{a3} pK_{a2} pK_{a3} pK_{a1} pK_{a2}

When pH > pK_{a3}, A^{3-} is dominant

When pH < pK_{a1} , H3A is dominant



The general form of α for the polyprotic acid H_nA is

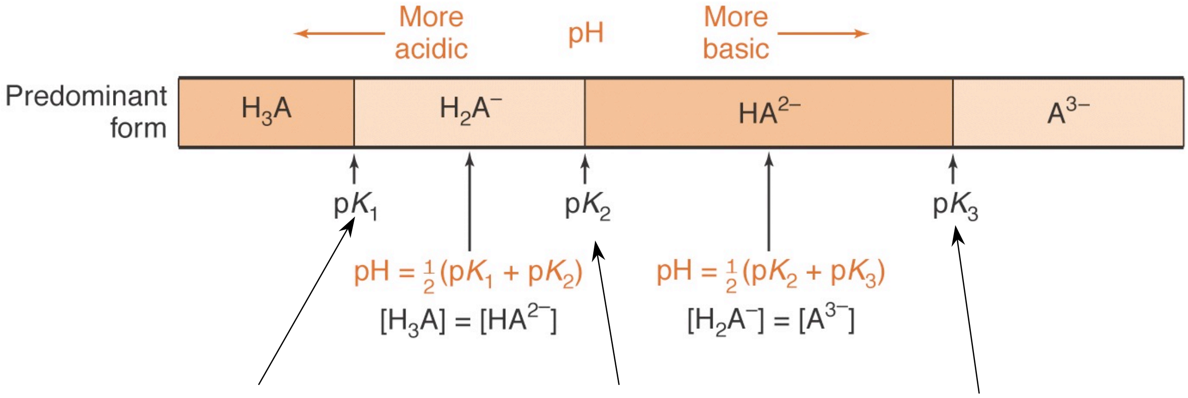
$$\alpha_{H_nA} = \frac{[H^+]^n}{D}$$

$$\alpha_{H_{n-1}A} = \frac{K_1[H^+]^{n-1}}{D}$$

$$\alpha_{H_{n-j}A} = \frac{K_1K_2 \ldots K_j[H^+]^{n-j}}{D}$$

where $D = [H^+]^n + K_1[H^+]^{n-1} + K_1K_2[H^+]^{n-2} + \cdots + K_1K_2K_3 \cdots K_n$.

Approximations:



$[H_3A] = [H_2A^-]$ $[H_2A^-] = [HA^{2-}]$ $[HA^{2-}] = [A^{3-}]$