11/28/05

- weak acids
- polyprotic acids
- polyelectrolytes

$\boxed{\text{See SAB pp 257-262}}$

General weak acid dissociation $HA \rightleftharpoons H^+ + A^-$

Since we can define

$$\mu_j = \underbrace{\mu_j^\circ}_{\text{includes ionic strength contributions}} + RT\ln C_j$$

Then dissociation constant is

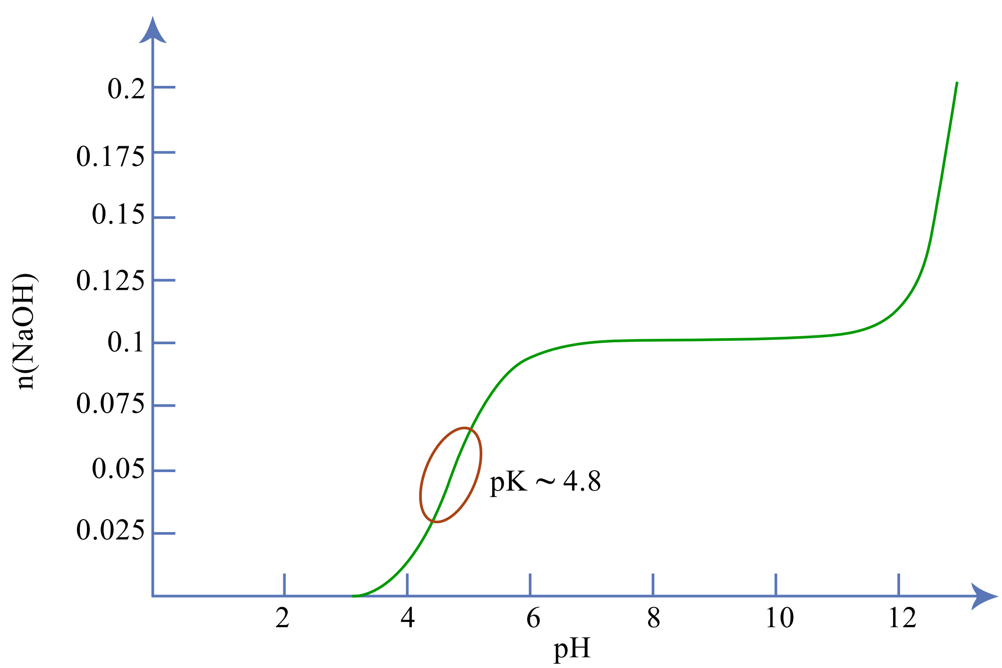
$$K = \frac{[H^+][A^-]}{[HA]} \Rightarrow -\log K = -\log[H^+] - \log\frac{[A^-]}{[HA]}$$

rearrange

$$\boxed{pH_c = pK + \log\frac{[A^-]}{[HA]}}$$ Henderson-Hasselback Eq^n

pK = pH where acid is 1/2 dissociated or $[A^-] = [HA]$

Weak acids buffer best at ± 1 pK



Titration of acetic acid with a concentrated solution of sodium hydroxide. The number of moles of NaOH added to a liter of 0.10 M acetic acid represented by n.

Figure by MIT OCW.

Example: Acetate Buffer $H\underbrace{Ac}_{\text{acetate}}$ $pK = 4.76$ ($25°C$, $I=0$)

What is the pH of a solution made with
1mM HAc + 2mM NaAc @ 25c?

$[Ac^-] \approx NaAc$ (complete dissociation)
$[HA] \approx HAc$ (negligible dissociation compared to NaAc)

$$pH_e = pK + \log\frac{2}{1} = 4.76 + 0.3 = 5.0$$

$$[H^+] = 10^{-5} \Rightarrow [OH^-] = 10^{-9}$$

Must have $Na^+ + H^+ = Ac^- + OH^-$

$$2\times10^{-3} + 5\times10^{-5} = ? + 10^{-9}$$

$Ac^- \approx 2\times10^{-5} \Rightarrow$ original assumption ok

---

Polyprotic Acid: Phosphate (Phosphate Buffered Saline)
Formal notation for 3 possible dissociation constants

① $HPO_4^{=} \rightleftharpoons PO_4^{3-} + H^+$ $\quad K_1 = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{=}]}$

② $H_2PO_4^- \rightleftharpoons HPO_4^{=} + H^+$ $\quad K_2 = \dfrac{[H^+][HPO_4^{=}]}{[H_2PO_4]}$

③ $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ $\quad K_3 = \dfrac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

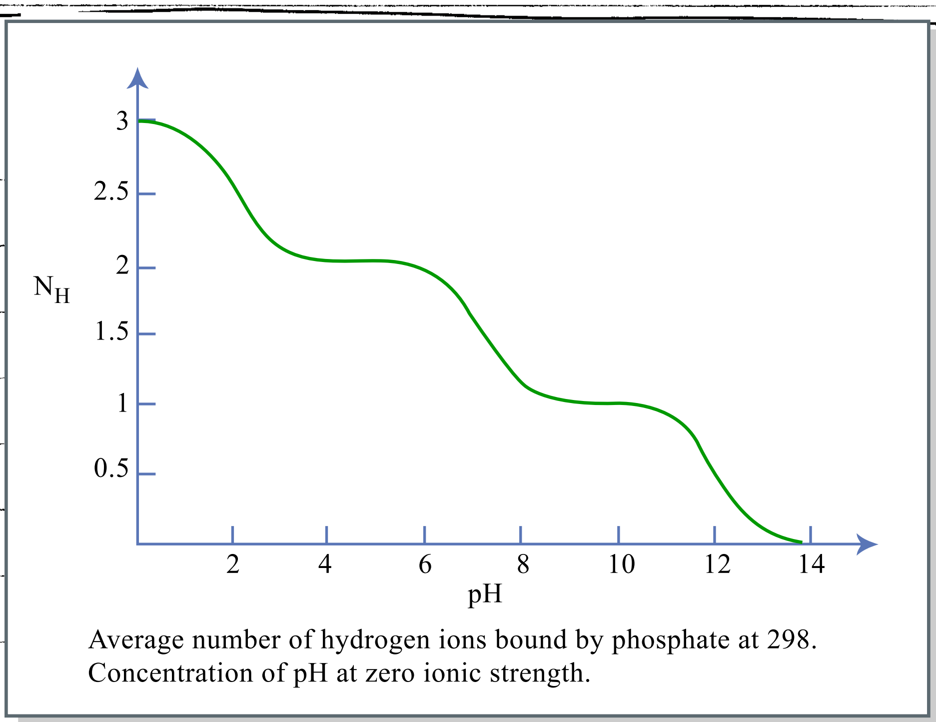
Average # protons per P

$$\bar{N}_H = \frac{[HPO_4^{=}] + 2[H_2PO_4^-] + 3[H_3PO_4]}{[PO_4^{3-}] + [HPO_4^{=}] + [H_2PO_4^-] + [H_3PO_4]}$$

Using $[PO_4^{3-}] = K_1 \frac{[HPO_4^{2-}]}{[H^+]}$ ETC

sub in K's

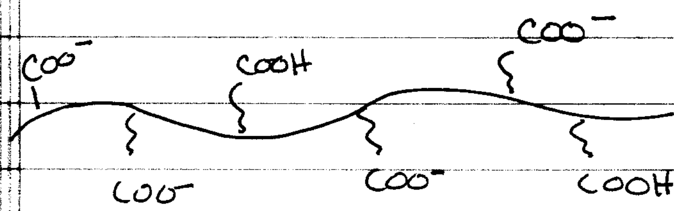
$$\boxed{\bar{N}_H = \frac{[H^+]/K_1 + 2[H^+]^2/K_1K_2 + 3[H^+]^3/K_1K_2K_3}{1 + [H^+]/K_1 + [H^+]^2/K_1K_2 + [H^+]^3/K_1K_2K_3}}$$

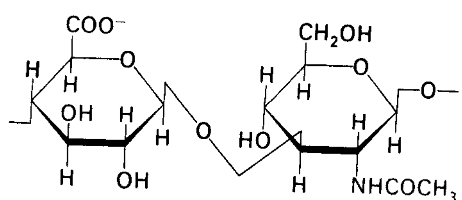


Average number of hydrogen ions bound by phosphate at 298.
Concentration of pH at zero ionic strength.

Figure by MIT OCW.

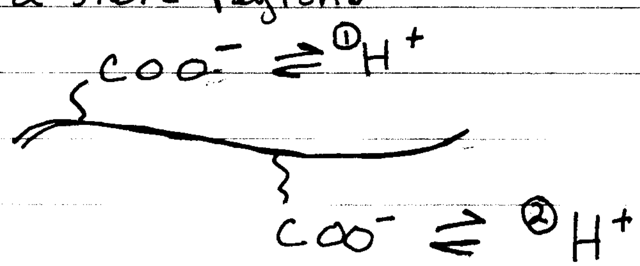
Polyelectrolytes – I   Hyaluronic acid





Hyaluronate

Relationship between microscopic & macroscopic eq$^{\underline{m}}$ constants.
In hyaluronate ⇒ all carboxylates are equivalent
Consider a short region:



Protons called "1" & "2" for accounting

microscopic K's are the same (carboxyls are equivalent)

$$K = \frac{[{}^1H^+][{}^2HA^-]}{[{}^1HA^2H]} = \frac{[{}^2H^+][{}^1HA^-]}{[{}^1HA^2H]} = \frac{[{}^1H^+][A^=]}{[{}^1HA^-]} = \frac{[{}^2H^+][A^=]}{[{}^2HA^-]}$$

As with phosphate ⇒

Macroscopic constants

$HA^- \rightleftharpoons H^+ + A^=$ $\qquad K_1 = \dfrac{[H^+][A^=]}{[HA^-]}$

$H_2A \rightleftharpoons H^+ + HA^-$ $\qquad K_2 = \dfrac{[H^+][HA^-]}{[H_2A]}$

Write macroscopic in terms of individual

$$K_1 = \frac{[H^+][A^=]}{\underbrace{[{}^1HA^-] + [{}^2HA^-]}_{\text{"[HA]"}}} = \frac{1}{\frac{1}{K} + \frac{1}{K}} = K/2$$

$$K_2 = \frac{[H^+][A^2H^-] + [A^1H^-]}{[{}^1HA^2H]} = 2K \Rightarrow = 4K_1$$

We derived earlier

$$\overline{N_H} = \frac{[H^+]/K_1 + 2[H^+]^2/K_1K_2}{1 + [H^+]/K_1 + [H^+]^2/K_1K_2}$$

sub in $K_1 = K/2 \quad K_2 = 2K$

$$\overline{N_H} = \frac{2[H^+]/K}{1 + [H^+]/K} \Rightarrow \text{when } [H^+] = K$$

1/2 of COO^- are protonated

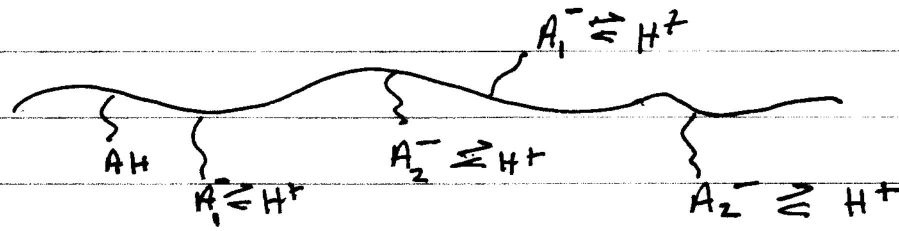
More general ⇒ long chain w/ N_{max} carboxyls

$$\overline{N_H} = N_{max}\,[H^+]/K \Big/ (1 + [H^+]/K)$$

So "K" always represents pH corresponding to 1/2 dissociation; ie, when pH = pK

$$\frac{\bar{N}_H}{N_{max}} = \frac{1}{2}$$

More general eg peptide



For different ionizable groups → eg.

aspartate	pK ~ 3.9	$-CH_2-COOH$
~~serine~~ tyrosine	pK ~ 10.9	$-CH_2-\phi-OH$
~~glutamine~~ lysine	pK ~ 10.8	$-CH_2-CH_2-CH_2-CH_2-NH_3^+$
glutamate	pK ~ 4.3	$-CH_2-CH_2-COOH$
cysteine	pK ~ 8.3	$-CH_2-SH$

General expression is

$$\bar{N}_H = \frac{n_1 [H^+]/K_1}{1 + [H^+]/K_1} + \frac{n_2 [H^+]/K_2}{1 + [H^+]/K_2} + \cdots$$

S 6

Effects of electrolyte –

Figure removed due to copyright reasons.
Please see:
Figure 30-1 in Silbey, R., R. Alberty, and M. Bawendi. *Physical Chemistry*. New York, NY: John Wiley & Sons, 2004. ISBN: 047121504X.

Figure removed due to copyright reasons.
Please see:
Figure 30-3 in Silbey, R., R. Alberty, and M. Bawendi. *Physical Chemistry*. New York, NY: John Wiley & Sons, 2004. ISBN: 047121504X.