Polyfunctional Species Equilibria

Compounds with more than one acidic/basic entities

$H_3PO_4, C_2O_4^{-2}, CO_3^{-2}$ etc.

$$H_3PO_4 = H_2PO_4^{-} + H^{+} \qquad K_{a1}$$
$$H_2PO_4^{-1} = HPO_4^{-2} + H^{+} \qquad K_{a2}$$
$$HPO_4^{-2} = PO_4^{-3} + H^{+} \qquad K_{a3}$$

$$H_3PO_4 = PO_4^{-3} + 3H^{+} \qquad K_a = K_{a1}K_{a2}K_{a3}$$
$$K_{a1} > K_{a2} > K_{a3}$$

$$PO_4^{-3} + H_2O = HPO_4^{-2} + OH^{-} \qquad K_{b1}$$
$$HPO_4^{-2} + H_2O = H_2PO_4^{-1} + OH^{-} \qquad K_{b2}$$
$$H_2PO_4^{-} + H_2O = H_3PO_4 + OH^{-} \qquad K_{b3}$$

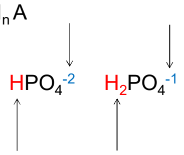
$$PO_4^{-3} + 3H_2O = H_3PO_4 + 3OH^{-}$$
$$K_b = K_{b1}K_{b2}K_{b3}$$
$$K_{b1} > K_{b2} > K_{b3}$$

$$K_{a1}K_{b3} = K_w$$
$$K_{a2}K_{b2} = K_w$$
$$K_{a3}K_{b1} = K_w$$

Amphiprotic Species:

Species with both *acidic* and *basic* properties.
Eg. HPO_4^{-2}, $H_2PO_4^{-1}$.

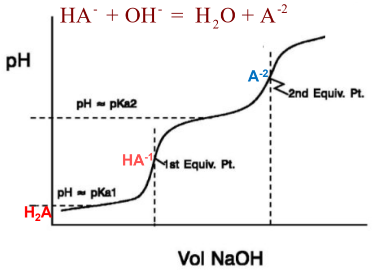
General Formula: H_nA


HPO_4^{-2} $H_2PO_4^{-1}$

Diprotic/dibasic species

$H_2A + OH^- = H_2O + HA^-$

$HA^- + OH^- = H_2O + A^{-2}$



Composition of fully protonated acid H_2A:

$H_2A = H^+ + HA^-$ first dissociation (major)

F initial concentration

(F - x) x x equilibrium concentration

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{F - x}$$ solve for x;

(If $K_{a1} >> K_{a2}$, *2nd dissociation, very small, minimal dissociation*)

$[H^+]$, $[HA^-]$ and $[H_2A]$ are calculable* (recall; x, F-x - previous chapter)

For; $HA^- = H^+ + A^{-2}$;second dissociation, A^{-2} (minor)

$$K_{a2} = \frac{[\cancel{H^+}][A^{-2}]}{[\cancel{HA^-}]}$$ solve for $[A^{-2}]*$

Composition of *amphiprotic* Na^+HA^- (mono-salt of H_2A) :

Existing equilibria; (formal conc. Na^+HA^- = F):

→ $\underline{HA^-} = \underline{H^+} + \underline{A^{-2}}$ K_{2a} (major)

→ $HA^- + H_2O = \underline{OH^-} + \underline{H_2}A$ $K_{b2} = \frac{K_w}{K_{1a}}$ (major)

$$K_{1a} = \frac{[H^+][HA^{-1}]}{[H_2A]}$$

$$K_{2a} = \frac{[H^+][A^{-2}]}{[HA^-]}$$

$$K_w = [H^+][OH^-]$$

$F_{HA} = F = [H_2A] + [HA^{-1}] + [A^{-2}]$ MB

$[H^+] + [Na^+] = [HA^-] + 2[A^{-2}] + [OH^-]$ CB $[Na^+]=F$

$[H^+] + F = [HA^-] + 2[A^{-2}] + [OH^-]$

$$[H^+] = \sqrt{\frac{K_{1a}K_{2a}F + K_{1a}K_w}{K_{1a} + F}}$$ ←

$$[H^+] = \sqrt{\frac{K_{2a}F + K_w}{1 + F/K_{1a}}}$$ division; K_{1a}

For $F/K_{1a} >> 1$ and $FK_{2a} >> K_w$ simplification

$$\boxed{[H^+] = \sqrt{K_{1a}K_{2a}}} \leftarrow pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Composition of Na_2A (salt) (salt of H_2A, F) :

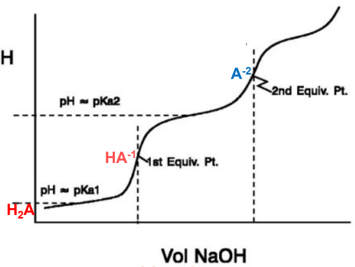
$A^{-2} + H_2O = OH^- + HA^-$ major K_{b1}

$$K_{b1} = \frac{[OH^-][HA^{-1}]}{[A^{-2}]} = \frac{[OH^-]^2}{F_{A^{-2}} - [OH^-]}; \quad \text{note}: [OH^-] = [HA^{-1}]$$

$K_w = [H^+][OH^-]$; calculate pH using K_w

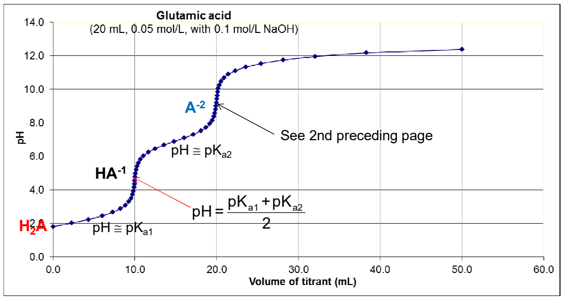
Further: $HA^- + H_2O = OH^- + H_2A$ $K_{b2} = \frac{K_w}{K_{1a}}$ (minor)

$$K_{1a} = \frac{[H^+][HA^{-1}]}{[H_2A]}$$



amphiprotic

HA^{-1} $[H^+] = \sqrt{K_{1a}K_{2a}}$ $pH = \frac{pK_{a1} + pK_{a2}}{2}$



amphiprotic

HA^{-1} $[H^+] = \sqrt{K_{1a}K_{2a}}$ $pH = \frac{pK_{a1} + pK_{a2}}{2}$

Triprotic/tribasic species

Composition of fully protonated acid H_3A (F):

$H_3A = H^+ + H_2A^-$ (major)

F initial concentration

(F - x) x x equilibrium concentration

$$K_{a1} = \frac{[H^+][H_2A^-]}{[H_3A]} = \frac{x^2}{F-x}$$ solve for x;

(If K_{a1} >> K_{a2} further equilibria are negligible.)

$[H^+]$, $[H_2A^-]$ and $[H_3A]$ are calculable*

Further: $H_2A^- = H^+ + HA^{-2}$ (lesser extent)

$$K_{a2} = \frac{[\cancel{H^+}][HA^{-2}]}{[\cancel{H_2A^-}]}$$ solve for $[HA^{-2}]$ *

$HA^{-2} = H^+ + A^{-3}$ (minor)

$$K_{a3} = \frac{[\cancel{H^+}][A^{-3}]}{[\cancel{HA^{-2}}]}$$ solve for $[A^{-3}]$

Composition of *amphiprotic* H_2A^- (salt) F :

Existing equilibria:

$H_2A^- = H^+ + HA^{-2}$ K_{2a}

$H_2A^- + H_2O = OH^- + H_3A$ $K_{b3} = \frac{K_w}{K_{1a}}$

$$K_{2a} = \frac{[H^+][HA^{-2}]}{[H_2A^-]}$$

$$K_{b3} = \frac{[OH^-][H_3A]}{[H_2A^-]}$$

$$K_w = [H^+][OH^-]$$

along with MB and CB equations give :

$$[H^+] = \sqrt{\frac{K_{1a}K_{2a}F + K_{1a}K_w}{K_{1a} + F}} \Rightarrow \boxed{[H^+] = \sqrt{K_{1a}K_{2a}}}$$ ←

for $F/K_{1a} >> 1$ and $FK_{2a} >> K_w$

pH of H_2A^- solution ~ $-\log\sqrt{K_{1a}K_{2a}}$

$$= \frac{pK_{1a} + pK_{2a}}{2}$$

pH of HA^{-2} (salt) solutions:

Amphiprotic; K_{2a} and K_{3a} describes the equilibria.

$$[H^+] = \sqrt{\frac{K_{2a}\enclose{circle}{K_{3a}}F + \enclose{circle}{K_{2a}}K_w}{K_{2a} + F}} \quad \longleftarrow$$

for $F/K_{2a} >> 1$ and $FK_{3a} >> K_w$

pH of H_2A^- solution ~ $-\log\sqrt{K_{2a}K_{3a}}$

$$\enclose{circle}{= \frac{pK_{2a} + pK_{3a}}{2}}$$

pH of A^{-3} (salt) solutions:

Treat as a simple hydrolysis of A^{-3}.

$$A^{-3} + H_2O = HA^{-2} + OH^-$$

F			initial concentration
(F - x)	x	x	equilibrium concentration

$$K_{b1} = \frac{[HA^{-2}][OH^-]}{[A^{-3}]} = \frac{x^2}{F - x}$$ solve for x;

Monoprotic systems – (approximate) calculation of buffer pH:

HA/A$^-$ or BH$^+$/B system
Considering the appropriate equilibria

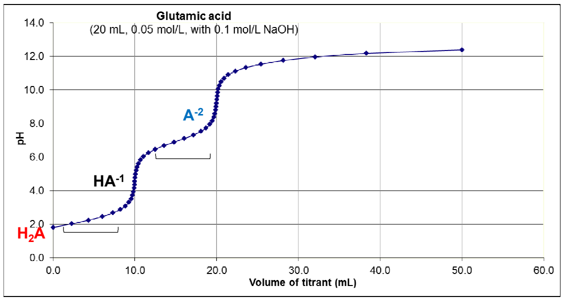
$$pH = \underset{\overset{\uparrow}{pK_{a,HA}}}{pK_a} + \log\frac{[A]}{[HA]} \longleftarrow \frac{[base]}{[acid]}$$

HA refers to the weak acid, it can be BH$^+$.

$$pH = \underset{\overset{\uparrow}{pK_{a,BH^+}}}{\overbrace{pK_w - pK_{b,B}}} + \log\frac{[B]}{[BH^+]} \longleftarrow \frac{[base]}{[acid]}$$

Henderson-Hasselbach Equation

Polyprotic Acid Buffers, Diprotic:



Polyprotic Acid Buffers:

1. H_2A/HA^- : K_{a1} based on diprotic WA
2. HA^-/A^{-2} : K_{a2}

$$pH = pK_{a1} + \log\frac{[HA^-]}{[H_2A]}$$

$$pH = pK_{a2} + \log\frac{[A^{-2}]}{[HA^-]}$$

Polyprotic Buffers:

1. H_3A/H_2A^- : K_{a1} based on triprotic WA
2. H_2A^-/HA^{-2} : K_{a2}
3. HA^{-2}/A^{-3} : K_{a3}

$$pH = pK_{a1} + \log\frac{[H_2A^-]}{[H_3A]}$$

$$pH = pK_{a2} + \log\frac{[HA^{-2}]}{[H_2A^-]}$$

$$pH = pK_{a3} + \log\frac{[A^{-3}]}{[HA^{-2}]}$$

Fractional Composition - Monoprotic Acid Case:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](F-[HA])}{[HA]}$$

$$[HA] = \frac{[H^+]F}{[H^+]+K_a} \quad \textit{by rearrangement}$$

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

$$\textit{similar approach} \quad \alpha_A = \frac{[A^-]}{[HA]+[A^-]} = \frac{[A^-]}{F} = \frac{K_a}{[H^+]+K_a}$$

$$\textit{or} \quad \alpha_A = 1-\alpha_{HA} = 1-\frac{[H^+]}{[H^+]+K_a} = \frac{[H^+]+K_a-[A^-]}{[H^+]+K} = \frac{K_a}{[H^+]+K_a}$$

or

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

$$[A^-] = \frac{FK_a}{[H^+]+K_a}$$

$$\alpha_A = \frac{[A^-]}{[HA]+[A^-]} = \frac{[A^-]}{F} = \frac{K_a}{[H^+]+K_a}$$

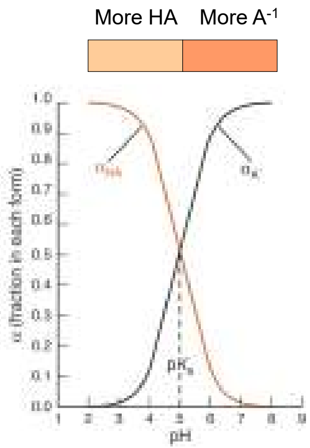
Also note the formal concentration F is;

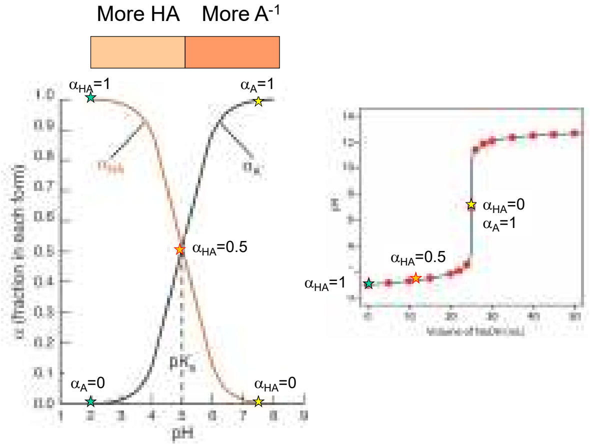
$$\mathrm{F} = [\mathrm{HA}]+[\mathrm{A}^{-1}] = [\mathrm{HA}]+\frac{\mathrm{K}_1[\mathrm{HA}]}{[\mathrm{H}^+]} = [\mathrm{HA}]\left(1+\frac{\mathrm{K}_1}{[\mathrm{H}^+]}\right)$$

$$F=[HA]+[A^{-1}]=[HA]+\frac{K_1[HA]}{[H^+]}=[HA]\left(1+\frac{K_1}{[H^+]}\right)$$

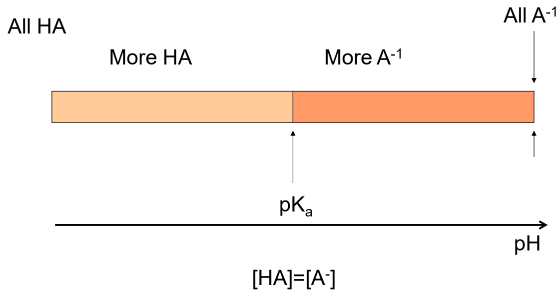
$$\alpha_{HA}=\frac{[H^+]^2}{[H^+]^2+[H^+]K_1}=\alpha_0$$

$$\alpha_{A^-}=\frac{K_1[H^+]}{[H^+]^2+[H^+]K_1}=\alpha_1$$





Composition, pH etc:



Fractional Composition - Diprotic acids.

Starting with the two acid dissociation equilibrium relations and mass balance for moiety (A), it can be shown that the total concentration of **A moiety**, say F, is;

$$F = [H_2A] + [HA^{-1}] + [A^{-2}] = [H_2A]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)$$

The above relationship along with expressions for H_2A, HA^- and A^{-2}, (please see text) leads to the fractional compositions as;

$$F = [HA] + [A^{-1}] = [HA] + \frac{K_1[HA]}{[H^+]} = [HA]\left(1 + \frac{K_1}{[H^+]}\right)$$

$$F = [H_2A] + [HA^{-1}] + [A^{-2}] = [H_2A]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)$$

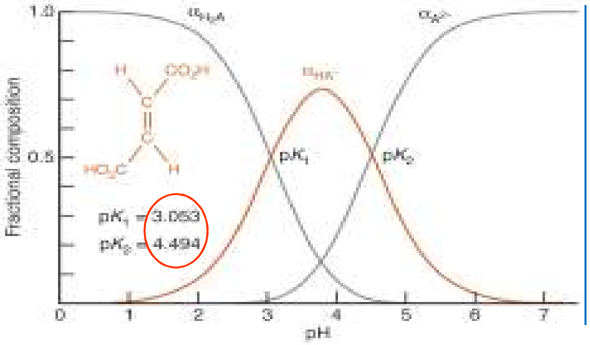
$$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} = \alpha_0$$

$$\alpha_{HA^-} = \frac{K_1[H^+]}{[H^+]^2 + [H^+]K_1 + K_1K_2} = \alpha_1$$

$$\alpha_{A^{-2}} = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2} = \alpha_2$$

$$\alpha_{HA} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1} = \alpha_0$$

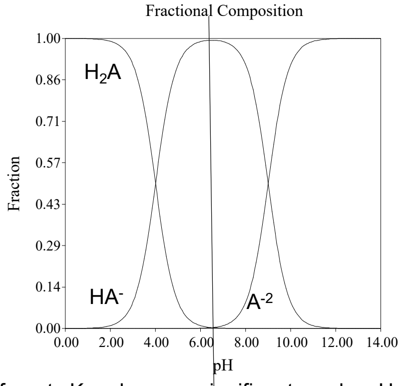
$$\alpha_{A^-} = \frac{K_1[H^+]}{[H^+]^2 + [H^+]K_1} = \alpha_1$$



Very close pK values; significant overlap of H_2A and A^{-2}.

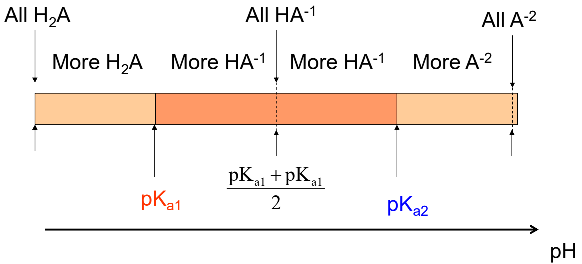
α_{HA} peaks before α_{H2A} completely vanishes, ...

pK_1=4.0
pK_2=9.0



Significantly different pK_a values; no significant overlap, H_2A & A^{-2}
α_{HA} peaks as α_{H2A} vanishes, ...

Composition, pH etc:



All H_2A

All HA^{-1}

All A^{-2}

More H_2A

More HA^{-1}

More HA^{-1}

More A^{-2}

pK_{a1}

$\frac{pK_{a1}+pK_{a1}}{2}$

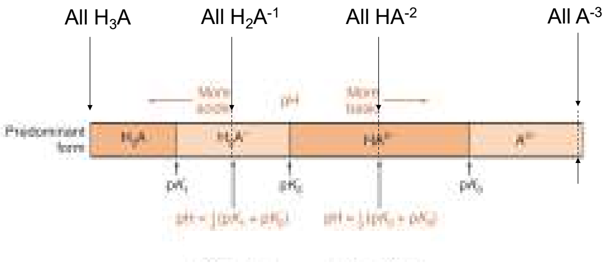
pK_{a2}

pH

$[H_2A]=[HA^-]$

$[HA^-]=[A^-]$

Composition, pH etc:



All H_3A

All H_2A^{-1}

All HA^{-2}

All A^{-3}

HA $$\alpha_{HA} = \frac{[H^+]}{[H^+]+K_1} = \alpha_0$$

$$\alpha_A = \frac{K_a}{[H^+]+K_1} = \alpha_1$$

H_2A $$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2+[H^+]K_1+K_1K_2} = \alpha_0$$

$$\alpha_{HA^-} = \frac{K_1[H^+]}{[H^+]^2+[H^+]K_1+K_1K_2} = \alpha_1$$

$$\alpha_{A^{-2}} = \frac{K_1K_2}{[H^+]^2+[H^+]K_1+K_1K_2} = \alpha_2$$

In general for H_nA.

$$\alpha_{H_nA} = \frac{[H^+]^n}{D} = \alpha_0$$

$$\alpha_{H_{n-1}A} = \frac{K_1[H^+]^{n-1}}{D} = \alpha_1$$

.

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

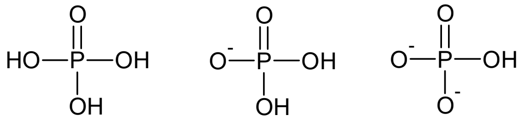
.

$$\alpha_A = \frac{K_1K_2..K_j[H^+]^{n-j}}{D} = \alpha_n$$

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

$$F = [HA] + [A^{-1}] = [HA] + \frac{K_1[HA]}{[H^+]} = [HA]\left(1 + \frac{K_1}{[H^+]}\right)$$

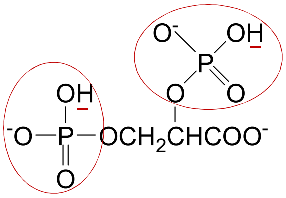
$$F = [H_2A] + [HA^{-1}] + [A^{-2}] = [H_2A]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)$$

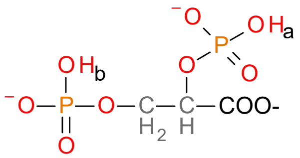


$pK_{a1} = 2.12$ $pK_{a2} = 7.21$ $pK_{a3} = 12.67$

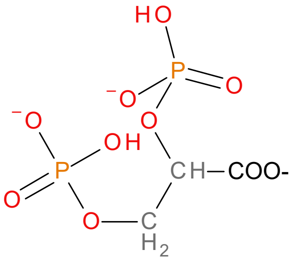
Microequilibrium constants

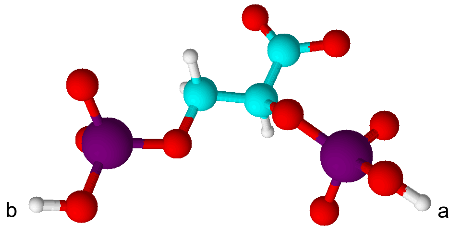
Species with two or more sites with similar dissociation constants.

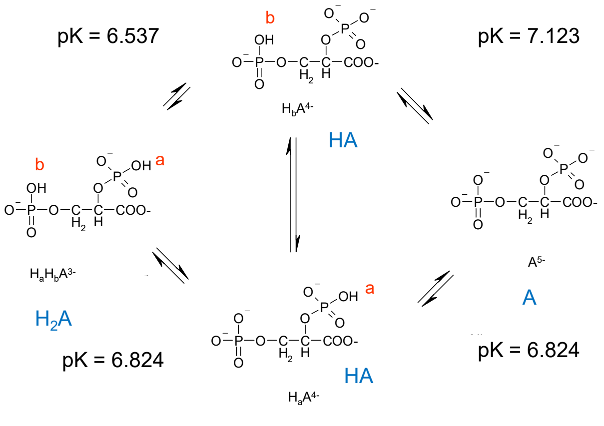




$H_aH_bA^{3-}$







Microscopic equilibrium constants

$$k_a = \frac{[H_bA^{-4}][H^+]}{[H_aH_bA^{-3}]} = 2.9\times10^{-7}$$ pK = 6.537

$$k_b = \frac{[H_aA^{-4}][H^+]}{[H_aH_bA^{-3}]} = 1.5\times10^{-7}$$ pK = 6.824

$$k_{ab} = \frac{[A^{-5}][H^+]}{[H_bA^{-4}]} = 7.5\times10^{-8}$$ pK = 7.123

$$k_{ba} = \frac{[A^{-5}][H^+]}{[H_aA^{-4}]} = 1.5\times10^{-7}$$ pK = 6.824

Macroscopic equilibrium constants

$$K_1 = \frac{[HA^{-4}][H^+]}{[H_2A^{-3}]}$$

$$K_1 = \frac{([H_aA^{-4}]+[H_bA^{-4}])[H^+]}{[H_aH_bA^{-3}]} = k_a + k_b$$

$$K_2 = \frac{[A^{-5}][H^+]}{([H_aA^{-4}]+[H_bA^{-4}])} = \frac{k_{ab}k_{ba}}{k_{ab}+k_{ba}}$$