Polyprotic acid-base equilibria (Ch 11)

To do calculations of diprotic acids and bases (Do Exercise 11-5)

- $_{a1}$, K_{a2} $_{b1}$, K_{b2} K_w

The acidic form

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•The intermediate form

To determine the fractional composition of individual species (Do Exercise 11-29 and study Box 10-1)

To calculate the isoelectric and isoionic pH values (Do Exercise 11-37 and 11-38)

Systematic treatment (9-1 & 9-2)

Diprotic acids and bases

Diprotic acid

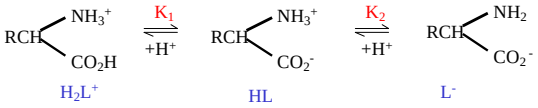
$H_2^+ \rightleftharpoons H^+ + HL$

$HL \rightleftharpoons H^+ + L^-$

K_{a_1} or $K_1 = \frac{[H^+][HL]}{[H_2L^+]}$

K_{a_2} or $K_2 = \frac{[H^+][L^-]}{[HL]}$

E.g. 1: Leucine hydrochloride [R = $(CH_3)_2CHCH_2$]



H_2L^+ HL L^-

E.g. 2: H_2CO_3 $\overset{K_1}{\underset{+H^+}{\rightleftharpoons}}$ HCO_3^- $\overset{K_2}{\underset{+H^+}{\rightleftharpoons}}$ CO_3^{2-}

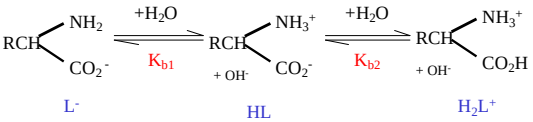
Diprotic acids and bases

Diprotic base

$L^- + H_2O \rightleftharpoons OH^- + HL$ $\quad K_{b_1} = \frac{[HL][OH^-]}{[L^-]}$

$HL + H_2O \rightleftharpoons OH^- + H_2L^+$ $\quad K_{b_2} = \frac{[H_2L^+][OH^-]}{[HL]}$

E.g. 1: Leucinate [R = $(CH_3)_2CHCH_2$]



L^- HL H_2L^+

E.g. 2: $CO_3^{2-} \overset{+H_2O}{\underset{K_{b1}}{\rightleftharpoons}} HCO_3^- + OH^- \overset{+H_2O}{\underset{K_{b2}}{\rightleftharpoons}} H_2CO_3 + OH^-$

Diprotic acids and bases

Recall

$K_1 = \frac{[H^+][HL]}{[H_2L^+]}$ $\quad K_{b_1} = \frac{[HL][OH^-]}{[L^-]}$

$K_2 = \frac{[H^+][L^-]}{[HL]}$ $\quad K_{b_2} = \frac{[H_2L^+][OH^-]}{[HL]}$

$K_1 K_{b_2} = \frac{[H^+][HL]}{[H_2L^+]} \cdot \frac{[H_2L^+][OH^-]}{[HL]} = [H^+][OH^-] = K_W$

$K_2 K_{b_1} = \frac{[H^+][L^-]}{[HL]} \cdot \frac{[HL][OH^-]}{[L^-]} = [H^+][OH^-] = K_W$

The acid form, H_2L^+

To calculate the concentrations of H_2L^+, HL, L^- and H^+ in 0.0500 M of leucine hydrochloride. ($K_1 = 4.69 \times 10^{-3}$ and $K_2 = 1.79 \times 10^{-10}$)

$H_2L^+ \rightleftharpoons H^+ + HL$ $\qquad$ $HL \rightleftharpoons H^+ + L^-$

0.0500-x		x	x		
0.0500-x-y		x+y	x-y	x-y	x+y y

$K_1 = \frac{[H^+][HL]}{[H_2L^+]} = \frac{(x+y)(x-y)}{0.0500-x-y}$ $\quad K_2 = \frac{[H^+][L^-]}{[HL]} = \frac{(x+y)y}{x-y}$

We make the approximation: y << x

$\therefore 4.69\times10^{-3} = \frac{x^2}{0.0500 - x}$ $\qquad x = 1.31\times10^{-2}$

$\therefore y = K_2 = 1.79\times10^{-10}$

So the approximation: y << x is justified.

The acid form, H_2L^+

(a) $[L^-] = y = 1.79\times10^{-10}\,M$

(b) $[H^+] = x + y \approx x = 1.31\times10^{-2}\,M$

$\therefore pH = -\log(1.31\times10^{-2}) = 1.883$

(c) $[HL] = x - y \approx x = 1.31\times10^{-2}\,M$

(d) $[H_2L^+] = 0.0500 - x - y \approx 0.0500 - x$

$= 5.00\times10^{-2} - 1.31\times10^{-2} = 3.69\times10^{-2}\,M$

The basic form, L^-

To calculate $[H_2L^+]$, $[HL]$, $[L^-]$ and $[H^+]$ in 0.0500 M of sodium leucinate. ($K_1 = 4.69 \times 10^{-3}$ and $K_2 = 1.79 \times 10^{-10}$)

$L^- + H_2O \rightleftharpoons OH^- + HL$ $\qquad$ $HL + H_2O \rightleftharpoons OH^- + H_2L^+$

0.0500-x		x	x			
0.0500-x-y		x+y	x-y	x-y	x+y	y

$$K_{b_1} = \frac{[HL][OH^-]}{[L^-]} \qquad K_{b_2} = \frac{[H_2L^+][OH^-]}{[HL]}$$

$$\frac{K_W}{K_2} = \frac{(x-y)(x+y)}{0.0500-x-y} \qquad \frac{K_W}{K_1} = \frac{y(x+y)}{x-y}$$

We make the approximation: y << x

$$\therefore \frac{1.0\times10^{-14}}{1.79\times10^{-10}} = \frac{x^2}{0.0500-x} \qquad \therefore y = \frac{1.0\times10^{-14}}{4.69\times10^{-3}}$$

$$x = 1.64\times10^{-3} \qquad = 2.13\times10^{-12}$$

So the approximation: y << x is justified.

The basic form, L^-

(*a*) $[H_2L^+] = y = 2.13\times10^{-12}\,M$

(*b*) $[OH^-] = x + y \approx x = 1.64\times10^{-3}\,M$

$$\therefore pH = -\log\left(\frac{1.0\times10^{-14}}{1.64\times10^{-3}}\right) = 11.22$$

(*c*) $[HL] = x - y \approx x = 1.64\times10^{-3}\,M$

(*d*) $[L^-] = 0.0500 - x - y \approx 0.0500 - x$

$= 5.00\times10^{-2} - 1.64\times10^{-3} = 4.84\times10^{-2}\,M$

The intermediate form, HL

To calculate $[H_2L^+]$, $[HL]$, $[L^-]$ and $[H^+]$ in 0.0500 M of leucine.

$HL \rightleftharpoons H^+ + L^-$ $\qquad$ $HL + H_2O \rightleftharpoons OH^- + H_2L^+$

0.0500-x		x	x	0.0500-y	y	y
0.0500-p		m	x	0.0500-p	n	y

Systematic treatment of equilibrium:

Charge balance

Electroneutrality of the solution

$$[H^+] + [H_2L^+] = [OH^-] + [L^-]$$

For H_2A, HA^- & A^{2-}

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

Mass balance

Conservation of atoms

$$F = [HL] + [H_2L^+] + [L^-] \approx [HL] \qquad F = [H_2A] + [HA^-] + [A^{2-}]$$

This is approximation 1 because HL is both a weak acid and weak base.

The intermediate form, HL

Re *call* $[H^+] + [H_2L^+] = [OH^-] + [L^-]$

$F \approx [HL]$ and the 3 equations for K_1, K_2 and K_w

We have 5 equations to solve for 5 unknowns: $[H_2L^+]$, $[HL]$, $[L^-]$, $[OH^-]$ and $[H^+]$

$$[H^+] + \frac{[HL][H^+]}{K_1} = \frac{K_W}{[H^+]} + \frac{K_2[HL]}{[H^+]}$$

Multiply by $K_1[H^+]$, $\qquad [H^+]^2K_1 + [HL][H^+]^2 = K_1K_W + K_1K_2[HL]$

$$[H^+]^2 = \frac{K_1K_2[HL] + K_1K_W}{K_1 + [HL]} \qquad or \qquad [H^+] = \sqrt{\frac{K_1K_2F + K_1K_W}{K_1 + F}}$$

$$\therefore [H^+] = \sqrt{\frac{(4.69\times10^{-3})(1.79\times10^{-10})(0.0500) + (4.69\times10^{-3})(1.0\times10^{-14})}{4.69\times10^{-3} + 0.0500}} = 8.7_6\times10^{-7}\,M$$

$$\therefore pH = -\log 8.7_6\times10^{-7} = 6.06$$

The intermediate form, HL

$$[H_2L^+] = \frac{[HL][H^+]}{K_1} = \frac{(8.76\times10^{-7})(0.0500)}{4.69\times10^{-3}} = 9.34\times10^{-6}\,M$$

$$[L^-] = \frac{[HL]K_1}{[H^+]} = \frac{(1.79\times10^{-10})(0.0500)}{8.76\times10^{-7}} = 1.02\times10^{-5}\,M$$

Since $[H_2L^+]$, $[L^-]$ << $[HL]$, approximation 1 is justified.

$HL \rightleftharpoons H^+ + L^-$ $\qquad$ $HL + H_2O \rightleftharpoons OH^- + H_2L^+$

0.0500-x		x	x			
0.0500-p		m	x	0.0500-p	n	y
0.0500		8.76×10^{-7}	1.02×10^{-5}	0.0500	1.14×10^{-8}	9.34×10^{-6}

The intermediate form, HL

Further approximations:

Approximation 2: *Since* $K_2F >> K_W$

or $K_1K_2F >> K_1K_W$

i.e. $(1.79\times10^{-10})(0.0500) = 8.95\times10^{-12} >> 1.0\times10^{-14}$

$$\therefore K_1K_2F + K_1K_W \approx K_1K_2F$$

The intermediate form, HL

Approximation 3: *Since* $K_1 << F$

i.e. $4.69\times10^{-3} << 0.0500$ $\quad \therefore K_1 + F \approx F$

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_W}{K_1 + F}} \approx \sqrt{\frac{K_1K_2F}{F}} = \sqrt{K_1K_2}$$

$$\therefore -\log[H^+] = -\frac{1}{2}(\log K_1 + \log K_2) \quad or \quad pH = \frac{1}{2}(pK_1 + pK_2)$$

$$\therefore [H^+] = \sqrt{(4.69\times10^{-3})(1.79\times10^{-10})} = 9.1_6\times10^{-7} M \quad (cf \quad 8.7_6\times10^{-7} M)$$

$$\therefore pH = -\log 9.1_6\times10^{-7} = 6.04 \qquad (cf \quad 6.06)$$

Fractional composition of monoprotic systems

Mass balance: $F = [HA] + [A^-]$

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

$$= [HA]\left(\frac{[H^+] + K_a}{[H^+]}\right)$$

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

Note that $\alpha_{A^-} + \alpha_{HA} = 1$

$$\therefore \alpha_{NH_4^+} = \frac{10^{-7.0}}{10^{-7.0} + 10^{-9.24}} = 0.99$$

Fractional composition of monoprotic systems

Fig 11-2: Plot α_{HA} and α_{A^-} versus -log[H^+] or pH to show the change of fractional composition with pH

Fractional composition of diprotic systems

Mass balance: $F = [H_2A] + [HA^-] + [A^{2-}]$

$$= [H_2A] + \frac{K_1[H_2A]}{[H^+]} + \frac{K_1K_2[H_2A]}{[H^+]^2} \qquad \because \quad K_1 = \frac{[H^+][HA^-]}{[H_2A]}$$

$$= [H_2A]\left(\frac{[H^+]^2 + [H^+]K_1 + K_1K_2}{[H^+]^2}\right) \qquad and \quad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

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

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

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

Note that $\alpha_{A^{2-}} + \alpha_{HA^-} + \alpha_{H_2A} = 1$

Fractional composition of diprotic systems

Fig 11-3: Plot α_{H2A}, α_{HA^-} and α_{A2^-} versus -log[H^+] or pH to show the change of fractional composition with pH

Fractional composition of a hexaprotic acid: EDTA

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{F} = \frac{K_1K_2K_3K_4K_5K_6}{[H^+]^6 + [H^+]^5K_1 + [H^+]^4K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^2K_1K_2K_3K_4 + [H^+]K_1K_2K_3K_4K_5 + K_1K_2K_3K_4K_5K_6}$$

Fig 13-6: Fractional composition diagram for EDTA

Isoelectric and isoionic points

Isoionic pH is the pH obtained when the pure neutral polyprotic acid (the neutral zwitterion) is dissolved in water, e.g. the intermediate form: HL.

i.e $[\ ^{+}] = \sqrt{\dfrac{K_1K_2\ \ + K\ K_W}{_1 + F}}$ Here, $[H_2L^+] \neq\ \ ^-]$

Isoelectric
polyprotic acid is zero, i.e., $[H_2L^+]$ [L

$$[H^+] = \sqrt{K_1K_2} \qquad or \qquad pH = \frac{1}{2}\left(pK_1 + pK_2\right)$$

For 0.10 M of alanine, isoionic pH = 6.12 and isoelectric pH = 6.11.

See Table 11-1 for pKa values of amino acids.

One application is to separate proteins using isoelectric focusing (IEF).