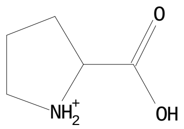
Solutions - Chapter 10

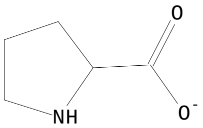
3.



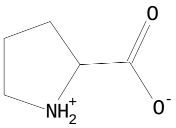
Proline: $pK_{a1} = 1.952\ (CO_2H)$

$pK_{a2} = 10.640\ (NH_2)$

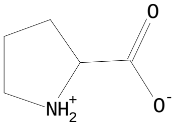
The stronger base is associated with K_{b1}; thus



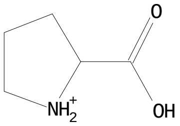
+ H^+ =



stronger base



+ H^+ =



weaker base

$pK_{1a} := 1.952 \qquad pK_{2a} := 10.640 \qquad pK_w \equiv 14$

For a polyprotic acid: $K_{na} \cdot K_{mb} = K_w$ and for a diprotic acid $na + mb = 3$

$$\log(K_{na}) + \log(K_{mb}) = \log(K_w)$$

$$pK_{na} + pK_{mb} = pK_w$$

$$pK_{2b} := pK_w - pK_{1a} \qquad pK_{2b} = 12.048$$

$$pK_{1b} := pK_w - pK_{2a} \qquad pK_{1b} = 3.36$$

4. (a) Diprotic acid dissociates, $K_1 >> K_2$ thus the first equilibrium is dominant, determines the concentrations of all species. If x mol/l is dissociated according to the equilibrium;

$$H_2A + H_2O = HA^- + H_3O^+$$

$$F_{H2A} - x \qquad x \qquad x$$

$F_{H2A} := 0.100 \qquad K_{1a} := 1.00 \cdot 10^{-4} \qquad K_{2a} := 1.00 \cdot 10^{-8}$

$K_{1a} = \frac{C_{HA} \cdot C_{H3O}}{C_{H2A}}$ Substitutes as: $K_{1a} = \frac{x \cdot x}{F_{H2A} - x}$

$K_{1a} = \frac{x \cdot x}{F_{H2A} - x}$ has solution(s) $\begin{pmatrix} \frac{-1}{2} \cdot K_{1a} - \frac{1}{2} \cdot \sqrt{K_{1a}} \cdot \sqrt{K_{1a} + 4 \cdot F_{H2A}} \\ \frac{-1}{2} \cdot K_{1a} + \frac{1}{2} \cdot \sqrt{K_{1a}} \cdot \sqrt{K_{1a} + 4 \cdot F_{H2A}} \end{pmatrix}$

$x := \frac{-1}{2} \cdot K_{1a} + \frac{1}{2} \cdot \sqrt{K_{1a}} \cdot \sqrt{K_{1a} + 4 \cdot F_{H2A}}$

$pH := -\log(x)$ $pH = 2.5069$

$C_{H2A} := F_{H2A} - x$ $C_{H2A} = 0.0969$

Concentration of HA- is nearly equal to x, since the second dissociation is much lower compared to the first. Fro the equilibrium where $[A^{-2}] = y$;

$HA^- + H_2O = A^{-2} + H_3O^+$

Equilibrium concentrations x y x

$F_{HA} := x$

$K_{2a} = \frac{C_{AA} \cdot C_{H3O}}{C_{HA}}$ substituting $K_{2a} = \frac{y \cdot x}{x}$

$K_{2a} = \frac{y \cdot x}{x}$ has solution(s) $y := K_{2a}$ $y = 1 \times 10^{-8}$ $C_{AA} := 1.0 \cdot 10^{-8}$

b.This is the 'first neutralization point' of a dibasic acid, considering the two equilibria of the species HA^-;

$F_{HA} := 0.100$ $K_w := 1 \cdot 10^{-14}$

$C_{H3O} := \sqrt{\frac{K_{1a} \cdot K_{2a} \cdot F_{HA} + K_{1a} \cdot K_w}{K_{1a} + F_{HA}}}$

$C_{H3O} = 9.9951 \times 10^{-7}$ $pH := -\log(C_{H3O})$ $pH = 6.0002$

assume $C_{HA} := F_{HA}$

Using; $K_{1a} = \frac{C_{HA} \cdot C_{H3O}}{C_{H2A}}$ has solution(s) $C_{H2A} := C_{HA} \cdot \frac{C_{H3O}}{K_{1a}}$

$C_{H2A} = 9.9951 \times 10^{-4}$

Consider $K_{2a} = \frac{C_{AA} \cdot C_{H3O}}{C_{HA}}$ has solution(s) $C_{AA} := \frac{K_{2a}}{C_{H3O}} \cdot C_{HA}$ $C_{AA} = 1.0005 \times 10^{-3}$

c. Here A^{-2} hydrolyses as; $A^{-2} + H_2O = HA + OH^-$

Equilibrium concentrations; $F_{AA} - z$ z z

$F_{AA} := 0.100$ $K_{1b} := \frac{K_w}{K_{2a}}$

$K_{1b} = \frac{z \cdot z}{F_{AA} - z}$ has solution(s)

$$\begin{pmatrix} \frac{-1}{2} \cdot K_{1b} - \frac{1}{2} \cdot \sqrt{K_{1b}} \cdot \sqrt{K_{1b} + 4 \cdot F_{AA}} \\ \frac{-1}{2} \cdot K_{1b} + \frac{1}{2} \cdot \sqrt{K_{1b}} \cdot \sqrt{K_{1b} + 4 \cdot F_{AA}} \end{pmatrix}$$

$z := \frac{-1}{2} \cdot K_{1b} + \frac{1}{2} \cdot \sqrt{K_{1b}} \cdot \sqrt{K_{1b} + 4 \cdot F_{AA}}$ $z = 3.1573 \times 10^{-4}$

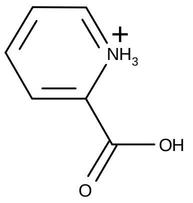
$pOH := -\log(z)$ $pH := 14 - pOH$ $pH = 10.4993$

$C_{H3O} := 10^{-pH}$ also, $C_{HA} := z$ $C_{HA} = 3.1573 \times 10^{-4}$

Using; $K_{1a} = \frac{C_{HA} \cdot C_{H3O}}{C_{H2A}}$ has solution(s) $C_{H2A} := C_{HA} \cdot \frac{C_{H3O}}{K_{1a}}$

$C_{H2A} = 1 \times 10^{-10}$

14. picolinic acid.
diprotic acid



$pK_{1a} := 1.01$

$pK_{2a} := 5.39$

To prepare the buffer, the equilibria involving mono acid salt (intermediate form, HA^-) must be used where the most acidic hydrogen is reacted to give a soluble salt, because the pK_{2a} is closer to the desired pH.

Required number of moles of picolinate is $0.100 \cdot \frac{mole}{liter} \cdot 0.10 \cdot liter = 0.01\,mole$

Starting with picolinic acid 0.01 mol of NaOH is reqired to convert to the monosodium salt.

Let the rest of the NaOH to bring the pH to 5.39 be x moles. Then x moles of A^{-2} will be formed and x moles of 0.010 moles of HA will be reacted. Applying the Hederson-Hasselbach equation for the relevant equilibrium;

$$HA^{-} = H^{+} + A^{-2}$$

$0.01 - x \quad 10^{-5.5} \quad x$ an alternate view.

$pH := 5.5 \qquad pK_{2a} := 5.39$ note; in HHE mole ratio = conc. ratio.

$$pH = pK_{2a} + \log\left(\frac{x}{0.010 - x}\right)$$ solved as below

$$\log\left(\frac{x}{0.010 - x}\right) = pH - pK_{2a}$$

$$\frac{x}{0.010 - x} = 10^{\left(pH - pK_{2a}\right)}$$ has solution(s) $$x := -1. \cdot \frac{10.^{\left(pH - 1. \cdot pK_{2a}\right)}}{\left[-100. - 100. \cdot 10.^{\left(pH - 1. \cdot pK_{2a}\right)}\right]}$$

$x = 5.6298 \times 10^{-3}$

Total moles of NaOH required is $0.01 \cdot mole + x \cdot mole = 0.0156\,mol$

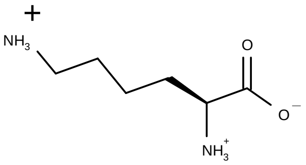
Volume (ml) of 0.1M NaOH $\frac{0.0156}{1.0} \cdot 1000 = 15.6$

Starting with diprotic form: ito a beaker add 0.010 mol (1.23g) of acid in 75 ml water, add 0.1M NaOH about 15.6ml, preferably monitoring with a pH sensing element. Cool, transfer into a 100ml volumetric flask, dilute to mark.

20. Lysine hydrochloride (chloride not shown) is a species engaging in two principal equilibria, in two principal directions. Dissociation at acidic H and hydrolysis at carboxylate. Full protonated form is H_3A. Thus it is an intermediate form of H_2A.

$pK_{3a} := 10.82$

$H_2A = H_2L^+ = Lys.H^+$



$pK_{1a} := 1.77$

$pK_{2a} := 9.07$

$K_1 := 10^{-pK_{1a}} \qquad K_2 := 10^{-pK_{2a}} \qquad F := 0.0100 \qquad K_3 := 10^{-pK_{3a}}$

K_1 and K_2 are the acid dissociation constants involved with the equilibria.

The species shown above undergoes hydrolysis (K_{1a}) and dissociation (K_{2a})

$C_H := \sqrt{\frac{K_1 \cdot K_2 \cdot F + K_1 \cdot K_w}{K_1 + F}}$ $H_2A=H_2L^+$; $H_3A=H_3L^+$; HL=HA; $L^- = A$

$C_H = 2.3159 \times 10^{-6}$ $pH := -\log(C_H)$ $pH = 5.6353$

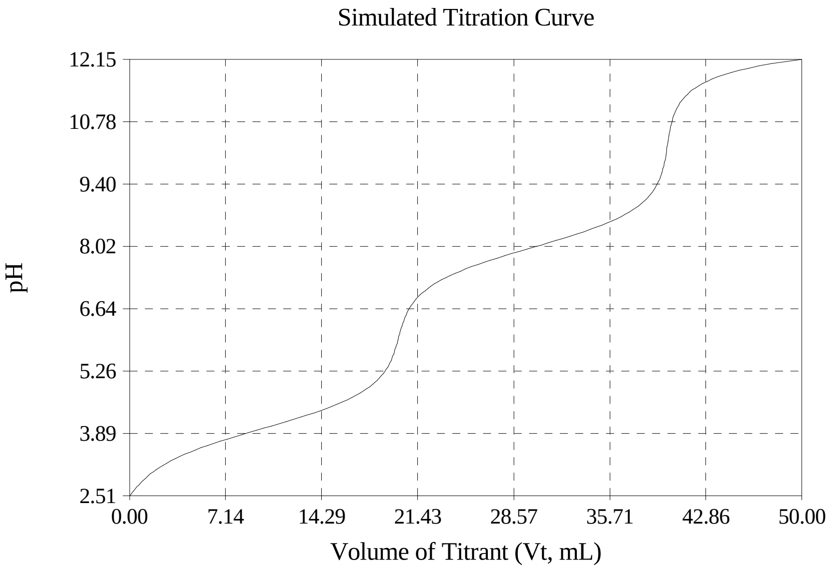
$C_{H2A} := F$ substance dissolved, extent of reactions not very large. $C_{H2A} = 0.01$

Consider other equilibria to calculate species concentrations.

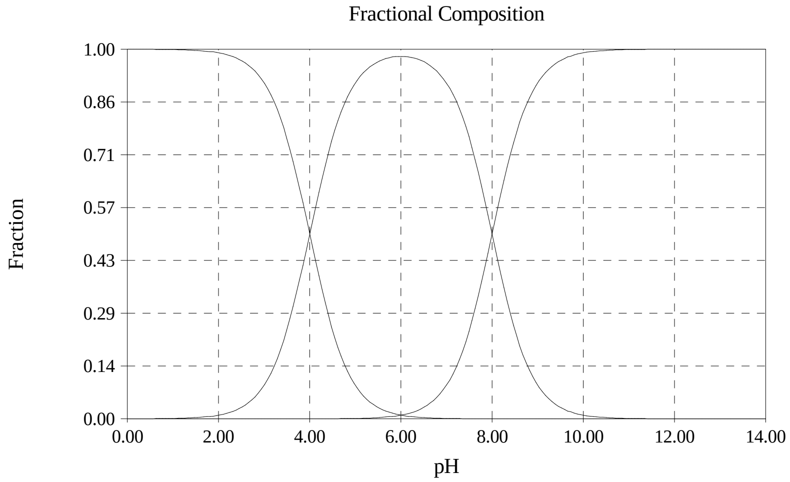
$K_1 = \frac{C_{H2A} \cdot C_H}{C_{H3A}}$ has solution(s) $C_{H3A} := C_{H2A} \cdot \frac{C_H}{K_1}$ $C_{H3A} = 1.3637 \times 10^{-6}$

$K_2 = \frac{C_{HA} \cdot C_H}{C_{H2A}}$ has solution(s) $C_{HA} := \frac{K_2}{C_H} \cdot C_{H2A}$ $C_{HA} = 3.6752 \times 10^{-6}$

$K_3 = \frac{C_H \cdot C_A}{C_{HA}}$ has solution(s) $C_A := \frac{K_3}{C_H} \cdot C_{HA}$ $C_A = 2.402 \times 10^{-11}$



24.



a simulated titration curve for a dibasic acid titrated with a strong base is shown above to facilitate visualization. As pH varies the concentration ration of the conjugate pair changes, or vice versa. Start: A^{-2} . End: H_2A and excess NaOH.

a . (reasoning with HHE or otherwise) pH = 4.00

b. pH = 8.00.   c. H_2A

d. HA^- e. A^{2-}.

25.

a. $pK_b := 5.00$

$pK_a := pK_w - pK_b$ $pK_a = 9$

b. pH = 9.00

c. BH^+

d. applying HHE approximation

$12.00 = 9.00 + \log(\text{ratio})$ has solution(s) $\text{ratio} := 1000.0$

28. $pK_{1b} := 4.00$ $pK_{2b} := 6.00$

$pK_{1a} := pK_w - pK_{2b}$ $pK_{2a} := pK_w - pK_{1b}$

$K_{1a} := 10^{-pK_{1a}}$ $K_{2a} := 10^{-pK_{2a}}$

need to know the C_H $C_H := 10^{-7}$

$$\alpha_{H2A} := \frac{C_H^{\,2}}{\left(C_H^{\,2} + C_H \cdot K_{1a} + K_{1a} \cdot K_{2a}\right)}$$

$\alpha_{H2A} = 0.909$

29. $K_{1a} := 10^{-8.85}$ $K_{2a} := 10^{-10.43}$

At pH=8.00 $C_H := 10^{-8}$

$$\alpha_{H2A} := \frac{C_H^{\,2}}{\left(C_H^{\,2} + C_H \cdot K_{1a} + K_{1a} \cdot K_{2a}\right)}$$

$\alpha_{H2A} = 0.8758$

$$\alpha_{HA} := \frac{C_H \cdot K_{1a}}{\left(C_H^{\,2} + C_H \cdot K_{1a} + K_{1a} \cdot K_{2a}\right)}$$

$\alpha_{HA} = 0.1237$

$$\alpha_{A} := \frac{K_{1a} \cdot K_{2a}}{\left(C_H^{\,2} + C_H \cdot K_{1a} + K_{1a} \cdot K_{2a}\right)}$$

$\alpha_A = 4.5964 \times 10^{-4}$

Work out the fractions at pH = 10.00 in a similar manner.

33. Sodium hydroxide reacts completely leaving the conjugate pair of cacodylic acid. The pH of the system is governed by this pair. Addition of a very small quantity of morphine do not affect the pH. However the pH will determine the concentration quotient of morphine conjugate pair.

Applying HHE cacodylic system:

$$pH := -\log\left(6.4\cdot 10^{-7}\right) + \log\left(\frac{.01\cdot 0.08}{0.01\cdot 0.10 - 0.01\cdot 0.08}\right)$$

$$pH = 6.7959$$

Applying HHE to morphine conjugate pair B/BH⁺:

$$K_{bB} := 1.6\cdot 10^{-6}$$

$$6.7959 = -\log\left(\frac{K_w}{K_{bB}}\right) + \log(ratio)$$ has solution(s) $$ratio := \frac{6.250e6\cdot K_w}{K_{bB}}$$

$ratio = 0.0391$ i.e. $\frac{C_B}{C_{BH}} = 0.0391$

$\frac{C_{BH}}{C_B} = \frac{1}{0.0391}$ yields $\frac{C_{BH}}{C_B} = 25.58$ $\frac{1}{0.0391} = 25.5754$

$fraction = \frac{C_{BH}}{C_B + C_{BH}}$ $fraction := \frac{25.58}{1 + 25.58}$ $fraction = 0.9624$