11.4 Considerar el ácido diprótico H_2A de K_{a1} = 1,00 x10^{-4} y K_{a2} = 1,00 x10^{-8}. Hallar el pH y las concentraciones de H_2A, HA^- y A^{2-} de a) H_2A 0,100 M, b) NaHA 0,100 M y c) Na_2A 0,100 M.

Respuesta/ a) pH = 2,507, [H_2A] = 0,097 mol/L, [HA^-] = 3,11 x10^{-3} mol/L y [A^{2-}] = 1,00 x10^{-8} mol/L
b) pH = 6,000, [H_2A] = 9,79 x10^{-4} mol/L, [HA^-] = 0,098 mol/L y [A^{2-}] = 9,81 x10^{-4} mol/L
c) pH = 10,497, [H_2A] = 1,01 x10^{-10} mol/L, [HA^-] = 3,17 x10^{-4} mol/L y [A^{2-}] = 0,100 mol/L

a)

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1{,}00\ x10^{-4}$$

	H_2A	$\rightleftharpoons$	H^+	+	HA^-
$Cn_{inicial}$	0,100		0		0
Cn_{final}	0,100 - x		x		x

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{(x)(x)}{0{,}100 - x} = 1{,}00\ x10^{-4}$$

$$x = 3{,}11\ x10^{-3}\ mol/L = [H^+] = [HA^-]$$

$$pH = 2{,}507$$

$$[H_2A] = 0{,}100 - x = 0{,}100\ mol/L - 3{,}11\ x10^{-3}\ mol/L = 0{,}097\ mol/L$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = 1{,}00\ x10^{-8}$$

$$K_{a2} = \frac{(3{,}11\ x10^{-3})[A^{2-}]}{(3{,}11\ x10^{-3})} = 1{,}00\ x10^{-8}$$

$$[A^{2-}] = 1{,}00\ x10^{-8}\ mol/L$$

b)

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

$$[H^+] = \sqrt{\frac{(1{,}00\ x10^{-4})(1{,}00\ x10^{-8})(0{,}100) + (1{,}00\ x10^{-4})(1{,}01\ x10^{-14})}{1{,}00\ x10^{-4} + 0{,}100}}$$

$$[H^+] = 1{,}00\ x10^{-6}\ mol/L$$

$$pH = 6{,}000$$

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1{,}00\ x10^{-4}$$

$$K_{a1} = \frac{(1{,}00\ x10^{-6})(0{,}100)}{[H_2A]} = 1{,}00\ x10^{-4}$$

$$[H_2A] = 1{,}00\ x10^{-3}\ mol/L$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = 1{,}00\ x10^{-8}$$

$$K_{a2} = \frac{(1{,}00\ x10^{-6})[A^{2-}]}{(0{,}100)} = 1{,}00\ x10^{-8}$$

$$[A^{2-}] = 1{,}00\ x10^{-3}\ mol/L$$

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

$$[HA^-] = 0{,}100\ mol/L - 1{,}00\ x10^{-3}\ mol/L - 1{,}00\ x10^{-3}\ mol/L = 0{,}098\ mol/L$$

con este valor de $[HA^-]$ recalculamos $[H^+]$ y pH,

y al hacerlo obtenemos

$$[H^+] = 9{,}99\ x10^{-7} mol/L \Longrightarrow pH = 6{,}000$$

con estos valores de $[HA^-]$ y $[H^+]$ recalculamos $[H_2A]$ y $[A^{2-}]$,

y al hacerlo obtenemos

$$[H_2A] = 9{,}79\ x10^{-4}\ mol/L$$

$$[A^{2-}] = 9{,}81\ x10^{-4}\ mol/L$$

con estos valores de $[H_2A]$ y $[A^{2-}]$ recalculamos $[HA^-]$,

y al hacerlo obtenemos

$$[HA^-] = 0{,}098\ mol/L \Longrightarrow \text{no debe repetirse el proceso}$$

c)

$$K_{a2} = 1{,}00\ x10^{-8} \Longrightarrow K_{b1} = 1{,}01\ x10^{-6}$$

$$K_{a1} = 1{,}00\ x10^{-4} \Longrightarrow K_{b2} = 1{,}01\ x10^{-10}$$

$$A^{2-} + H_2O \rightleftharpoons OH^- + HA^- \qquad K_{b1} = \frac{[OH^-][HA^-]}{[A^{2-}]} = 1{,}01\ x10^{-6}$$

	A^{2-}	$+\ H_2O$	$\rightleftharpoons$	OH^-	$+$	HA^-
$Cn_{inicial}$	0,100	---		0		0
Cn_{final}	0,100 - x	---		x		x

$$K_{b1} = \frac{[OH^-][HA^-]}{[A^{2-}]} = \frac{(x)(x)}{0{,}100 - x} = 1{,}01\ x10^{-6}$$

$$x = 3{,}17\ x10^{-4}\ mol/L = [OH^-] = [HA^-]$$

$$pOH = 3{,}499 \Longrightarrow pH = 10{,}497$$

$$[A^{2-}] = 0{,}100 - x = 0{,}100\ mol/L - 3{,}17\ x10^{-4}\ mol/L = 0{,}100\ mol/L$$

$$HA^- + H_2O \rightleftharpoons OH^- + H_2A \qquad K_{b2} = \frac{[OH^-][H_2A]}{[HA^-]} = 1{,}01\ x10^{-10}$$

$$K_{b2} = \frac{(3{,}17\ x10^{-4})[H_2A]}{(3{,}17\ x10^{-4})} = 1{,}01\ x10^{-10}$$

$$[H_2A] = 1{,}01\ x10^{-10}\ mol/L$$

11.5 Si al ácido malónico, $CH_2(CO_2H)_2$, lo designamos abreviadamente como H_2M, hallar el pH y las concentraciones de H_2M, HM^- y M^{2-} en a) H_2M 0,100 M, b) NaHM 0,100 M y c) Na_2M 0,100 M.

Respuesta/ a) pH = 1,951, $[H_2M]$ = 0,089 mol/L, $[HM^-]$ = 0,0112 mol/L y $[M^{2-}]$ = 2,01 x10^{-6} mol/L
b) pH = 4,276, $[H_2M]$ = 3,47 x10^{-3} mol/L, $[HM^-]$ = 0,093 mol/L y $[M^{2-}]$ = 3,53 x10^{-3} mol/L
c) pH = 9,346, $[H_2M]$ = 7,11 x10^{-12} mol/L, $[HM^-]$ = 2,24 x10^{-5} mol/L y $[M^{2-}]$ = 0,100 mol/L

a)

$$H_2M \rightleftharpoons H^+ + HM^- \qquad K_{a1} = \frac{[H^+][HM^-]}{[H_2M]} = 1{,}42\ x10^{-3}$$

	H_2M	$\rightleftharpoons$	H^+	+	HM^-
$Cn_{inicial}$	0,100		0		0
Cn_{final}	0,100 - x		x		x

$$K_{a1} = \frac{[H^+][HM^-]}{[H_2M]} = \frac{(x)(x)}{0{,}100 - x} = 1{,}42\ x10^{-3}$$

$$x = 0{,}0112\ mol/L = [H^+] = [HM^-]$$

$$pH = 1{,}951$$

$$[H_2M] = 0{,}100 - x = 0{,}100\ mol/L - 0{,}0112\ mol/L = 0{,}089\ mol/L$$

$$HM^- \rightleftharpoons H^+ + M^{2-} \qquad K_{a2} = \frac{[H^+][M^{2-}]}{[HM^-]} = 2{,}01\ x10^{-6}$$

$$K_{a2} = \frac{(0{,}0112)[A^{2-}]}{(0{,}0112)} = 2{,}01\ x10^{-6}$$

$$[M^{2-}] = 2{,}01\ x10^{-6}\ mol/L$$

b)

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HM^-] + K_{a1}K_w}{K_{a1} + [HM^-]}} \Rightarrow \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

$$[H^+] = \sqrt{\frac{(1{,}42\ x10^{-3})(2{,}01\ x10^{-6})(0{,}100) + (1{,}42\ x10^{-3})(1{,}01\ x10^{-14})}{1{,}42\ x10^{-3} + 0{,}100}}$$

$$[H^+] = 5{,}30\ x10^{-5}\ mol/L$$

$$pH = 4{,}276$$

$$H_2M \rightleftharpoons H^+ + HM^- \qquad K_{a1} = \frac{[H^+][HM^-]}{[H_2M]} = 1{,}42\ x10^{-3}$$

$$K_{a1} = \frac{(5{,}30\ x10^{-5})(0{,}100)}{[H_2M]} = 1{,}42\ x10^{-3}$$

$$[H_2M] = 3{,}73\ x10^{-3}\ mol/L$$

$$HM^- \rightleftharpoons H^+ + M^{2-} \qquad K_{a2} = \frac{[H^+][M^{2-}]}{[HM^-]} = 2{,}01\ x10^{-6}$$

$$K_{a2} = \frac{(5{,}30\ x10^{-5})[M^{2-}]}{(0{,}100)} = 2{,}01\ x10^{-6}$$

$$[M^{2-}] = 3{,}79\ x10^{-3}\ mol/L$$

$$[HM^-] = F - [H_2M] - [M^{2-}]$$

$$[HM^-] = 0{,}100\ mol/L - 3{,}73\ x10^{-3}\ mol/L - 3{,}79\ x10^{-3}\ mol/L = 0{,}092\ mol/L$$

con este valor de $[HM^-]$ recalculamos $[H^+]$ y pH,

y al hacerlo obtenemos

$$[H^+] = 5{,}30\ x10^{-5} mol/L \Longrightarrow pH = 4{,}276$$

con estos valores de $[HA^-]$ y $[H^+]$ recalculamos $[H_2M]$ y $[M^{2-}]$,

y al hacerlo obtenemos

$$[H_2M] = 3{,}43\ x10^{-3}\ mol/L$$

$$[M^{2-}] = 3{,}49\ x10^{-3}\ mol/L$$

con estos valores de $[H_2M]$ y $[M^{2-}]$ recalculamos $[HM^-]$,

y al hacerlo obtenemos

$$[HM^-] = 0{,}093\ mol/L$$

si repetimos de nuevo el proceso obtenemos

$$[H_2M] = 3{,}47\ x10^{-3}\ mol/L$$

$$[M^{2-}] = 3{,}53\ x10^{-3}\ mol/L$$

$$[HM^-] = 0{,}093\ mol/L$$

∴ hasta aquí es suficiente

c)

$$K_{a2} = 2{,}01\ x10^{-6} \Longrightarrow K_{b1} = 5{,}02\ x10^{-9}$$

$$K_{a1} = 1{,}42\ x10^{-3} \Longrightarrow K_{b2} = 7{,}11\ x10^{-12}$$

$$M^{2-} + H_2O \rightleftharpoons OH^- + HM^- \qquad K_{b1} = \frac{[OH^-][HM^-]}{[M^{2-}]} = 5{,}02\ x10^{-9}$$

	M^{2-}	$+ H_2O \rightleftharpoons$	OH^-	$+$	HM^-
$Cn_{inicial}$	0,100	---	0		0
Cn_{final}	0,100 - x	---	x		x

$$K_{b1} = \frac{[OH^-][HM^-]}{[M^{2-}]} = \frac{(x)(x)}{0{,}100 - x} = 5{,}02\ x10^{-9}$$

$$x = 2{,}24\ x10^{-5}\ mol/L = [OH^-] = [HM^-]$$

$$pOH = 4{,}650 \Longrightarrow pH = 9{,}346$$

$$[M^{2-}] = 0{,}100 - x = 0{,}100\ mol/L - 2{,}24\ x10^{-5}\ mol/L = 0{,}100\ mol/L$$

$$HM^- + H_2O \rightleftharpoons OH^- + H_2M \qquad K_{b2} = \frac{[OH^-][H_2M]}{[HM^-]} = 7{,}11\ x10^{-12}$$

$$K_{b2} = \frac{(2{,}24\ x10^{-5})[H_2M]}{(2{,}24\ x10^{-5})} = 7{,}11\ x10^{-12}$$

$$[H_2M] = 7{,}11\ x10^{-12}\ mol/L$$

11.6 Calcular el pH de una disolución de piperacina 0,300 M. Calcular la concentración de cada una de las formas de la piperacina en esta disolución.

Respuesta/ pH = 11,599, [B] = 0,296 mol/L, $[BH^+]$ = 4,01 x10^{-3} mol/L y $[BH_2^{2+}]$ = 2,17 x10^{-9} mol/L

$$K_{a2} = 1{,}86\ x10^{-10} \Longrightarrow K_{b1} = 5{,}43\ x10^{-5}$$

$$K_{a1} = 4{,}65\ x10^{-6} \Longrightarrow K_{b2} = 2{,}17\ x10^{-9}$$

Representamos piperacina como B

$$B + H_2O \rightleftharpoons OH^- + BH^+ \qquad K_{b1} = \frac{[OH^-][BH^+]}{[B]} = 5{,}43\ x10^{-5}$$

	B	+ H_2O ⇌	OH^-	+	BH^+
$Cn_{inicial}$	0,300	---	0		0
Cn_{final}	0,300- x	---	x		x

$$K_{b1} = \frac{[OH^-][BH^+]}{[B]} = \frac{(x)(x)}{0{,}300 - x} = 5{,}43\ x10^{-5}$$

$$x = 4{,}01\ x10^{-3}\ mol/L = [OH^-] = [BH^+]$$

$$pOH = 2{,}397 \Longrightarrow pH = 11{,}599$$

$$[B] = 0{,}300 - x = 0{,}300\ mol/L - 4{,}01\ x10^{-3}\ mol/L = 0{,}296\ mol/L$$

$$BH^+ + H_2O \rightleftharpoons OH^- + BH_2^{2+} \qquad K_{b2} = \frac{[OH^-][BH_2^{2+}]}{[BH^+]} = 2{,}17\ x10^{-9}$$

$$K_{b2} = \frac{(4{,}01\ x10^{-3})[BH_2^{2+}]}{(4{,}01\ x10^{-3})} = 2{,}17\ x10^{-9}$$

$$[BH_2^{2+}] = 2{,}17\ x10^{-9}\ mol/L$$

11.11 ¿Cuántos gramos de Na_2CO_3 (105,99 g/mol) se deben añadir a 5,00 g de $NaHCO_3$ (84,01 g/mol) para producir 100 mL de tampón de pH 10,000?

Respuesta/ 2,96 g de Na_2CO_3

$$5{,}00\ \text{g NaHCO}_3 * \frac{\text{mol NaHCO}_3}{84{,}01\ \text{g NaHCO}_3} \div 0{,}100\ \text{L} = 0{,}595\ \text{mol NaHCO}_3/\text{L}$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \qquad \text{K}_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4{,}69\ \text{x}10^{-11}$$

$$\text{pH} = \text{pK}_{a2} + \log\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$10{,}000 = 10{,}329 + \log\frac{[\text{CO}_3^{2-}]}{0{,}595}$$

$$[\text{CO}_3^{2-}] = 0{,}279\ \text{mol/L}$$

$$\frac{0{,}279\ \text{mol CO}_3^{2-}}{\text{L}} * \frac{1\ \text{mol Na}_2\text{CO}_3}{1\ \text{mol CO}_3^{2-}} * \frac{105{,}99\ \text{g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} * 0{,}100\ \text{L} = 2{,}96\ \text{g Na}_2\text{CO}_3$$

11.12 ¿Cuántos mL de NaOH 0,202 M se deben añadir a 25,0 mL de ácido salicílico 0,0233 M (2-hidroxibenzoico, 138,12 g/mol) para ajustar el pH a 3,500?

Respuesta/ 2,22 mL de NaOH 0,202 mol/L

$$25{,}0\ \text{mL} * \frac{0{,}0233\ \text{mmol ácido salicílico}}{\text{mL}} = 0{,}582\ \text{mmol ácido salicílico}$$

Representamos ácido salicílico como H_2A

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1{,}07\ x10^{-3}$$

Si tenemos "x" mmol de NaOH

	H_2A	+	OH^-	$\longrightarrow$	HA^-	+	H_2O
$mmol_{inicial}$	0,582		x		---		---
$mmol_{final}$	0,582 - x		---		x		---

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

$$3{,}500 = 2{,}971 + \log\frac{x}{0{,}582 - x}$$

$$x = 0{,}449\ \text{mmol NaOH}$$

$$\frac{0{,}449\ \text{mmol KOH}}{0{,}202\ \text{mmol KOH/mL}} = 2{,}22\ \text{mL}$$

11.14 ¿Cuántos gramos de Na_2SO_4 (142,04 g/mol) y de ácido sulfúrico (98,07 g/mol) se deben mezclar para obtener 1,00 L de tampón de pH 2,800, y una concentración total de azufre (= SO_4^{2-} + HSO_4^- + H_2SO_4) 0,200 M?

Respuesta/ 26,6 g de Na_2SO_4 y 1,31 g de H_2SO_4

Si tenemos "x" mol de H_2SO_4 y "y" mol de Na_2SO_4

	H_2SO_4	+	Na_2SO_4	$\longrightarrow$	$2NaHSO_4$
$mol_{inicial}$	x		y		---
mol_{final}	---		y - x		2x

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1{,}02\ x10^{-2}$$

$$pH = pK_{a2} + \log\frac{[SO_4^{2-}]}{[HSO_4^-]}$$

$$2{,}800 = 1{,}991 + \log\frac{y - x}{2x}$$

$$x + y = 0{,}200 \Longrightarrow y = 0{,}200 - x$$

$$2{,}800 = 1{,}991 + \log\frac{0{,}200 - 2x}{2x}$$

$$x = 0{,}0134 \text{ mol } H_2SO_4 \Longrightarrow y = 0{,}187 \text{ mol } Na_2SO_4$$

$$0{,}0134 \text{ mol } H_2SO_4 * \frac{98{,}07 \text{ g } H_2SO_4}{\text{mol } H_2SO_4} = 1{,}31 \text{ g } H_2SO_4$$

$$0{,}187 \text{ mol } Na_2SO_4 * \frac{142{,}04 \text{ g } Na_2SO_4}{\text{mol } Na_2SO_4} = 26{,}6 \text{ g } Na_2SO_4$$

11.17 a) Calcular el cociente $[H_3PO_4]/[H_2PO_4^-]$ en una disolución de KH_2PO_4 0,0500 M.
b) Hallar el mismo cociente para una disolución K_2HPO_4 0,0500 M.

Respuesta/ a) 2,78 x10^{-3}
b) 3,4 x10^{-8}

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7{,}11\ x10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_{a1} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6{,}32\ x10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_{a1} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 7{,}1\ x10^{-13}$$

a)

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

$$[H^+] = \sqrt{\frac{(7{,}11\ x10^{-3})(6{,}32\ x10^{-8})(0{,}050) + (7{,}11\ x10^{-3})(1{,}01\ x10^{-14})}{7{,}11\ x10^{-3} + 0{,}0500}}$$

$$[H^+] = 1{,}98\ x10^{-5}\ mol/L$$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(1{,}98\ x10^{-5})[H_2PO_4^-]}{[H_3PO_4]} = 7{,}11\ x10^{-3}$$

$$\frac{[H_3PO_4]}{[H_2PO_4^-]} = 2{,}78\ x10^{-3}$$

b)

$$[H^+] = \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}}$$

$$[H^+] = \sqrt{\frac{(6{,}32\ x10^{-8})(7{,}1\ x10^{-13})(0{,}0500) + (6{,}32\ x10^{-8})(1{,}01\ x10^{-14})}{6{,}32\ x10^{-8} + 0{,}0500}}$$

$$[H^+] = 2{,}4\ x10^{-10}\ mol/L$$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(2{,}4\ x10^{-10})[H_2PO_4^-]}{[H_3PO_4]} = 7{,}11\ x10^{-3}$$

$$\frac{[H_3PO_4]}{[H_2PO_4^-]} = 3{,}4\ x10^{-8}$$

11.19 Hallar el pH y la concentración de cada una de las especies de lisina en una disolución de lisina·HCl, monohidrocloruro de lisina, 0,0100 M.

Respuesta/ pH = 5,70, $[H_3L^{2+}]$ = 2,2 x10^{-6} mol/L, $[H_2L^+]$ = 0,0100 mol/L, [HL] = 4,2 x10^{-6} mol/L y $[L^-]$ = 4,2 x10^{-11} mol/L

Representamos lisina · HCl como H_2L^+

$$H_3L^{2+} \rightleftharpoons H^+ + H_2L^+ \qquad K_{a1} = \frac{[H^+][H_2L^+]}{[H_3L^{2+}]} = 9{,}1\ x10^{-3}$$

$$H_2L^+ \rightleftharpoons H^+ + HL \qquad K_{a2} = \frac{[H^+][HL]}{[H_2L^+]} = 8{,}3\ x10^{-10}$$

$$HL \rightleftharpoons H^+ + L^- \qquad K_{a3} = \frac{[H^+][L^-]}{[HL]} = 2{,}0\ x10^{-11}$$

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[H_2L^+] + K_{a1}K_w}{K_{a1} + [H_2L^+]}} \Rightarrow \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

$$[H^+] = \sqrt{\frac{(9{,}1\ x10^{-3})(8{,}3\ x10^{-10})(0{,}0100) + (9{,}1\ x10^{-3})(1{,}01\ x10^{-14})}{9{,}1\ x10^{-3} + 0{,}0100}}$$

$$[H^+] = 2{,}0\ x10^{-6}\ mol/L$$

$$pH = 5{,}70$$

$$H_3L^{2+} \rightleftharpoons H^+ + H_2L^+ \qquad K_{a1} = \frac{[H^+][H_2L^+]}{[H_3L^{2+}]} = 9{,}1\ x10^{-3}$$

$$K_{a1} = \frac{(2{,}0\ x10^{-6})(0{,}0100)}{[H_3L^{2+}]} = 9{,}1\ x10^{-3}$$

$$[H_3L^{2+}] = 2{,}2\ x10^{-6}\ mol/L$$

$$H_2L^+ \rightleftharpoons H^+ + HL \qquad K_{a2} = \frac{[H^+][HL]}{[H_2L^+]} = 8{,}3\ x10^{-10}$$

$$K_{a2} = \frac{(2{,}0\ x10^{-6})[HL]}{0{,}0100} = 8{,}3\ x10^{-10}$$

$$[HL] = 4{,}2\ x10^{-6}\ mol/L$$

$$HL \rightleftharpoons H^+ + L^- \qquad K_{a3} = \frac{[H^+][L^-]}{[HL]} = 2{,}0\ x10^{-11}$$

$$K_{a3} = \frac{(2{,}0\ x10^{-6})[L^-]}{4{,}2\ x10^{-6}} = 2{,}0\ x10^{-11}$$

$$[L^-] = 4{,}2\ x10^{-11}\ mol/L$$

$$[H_2L^+] = F - [H_3L^{2+}] - [HL] - [L^-]$$

$$[H_2L^+] = 0{,}0100\ mol/L - 2{,}2\ x10^{-6}\ mol/L - 4{,}2\ x10^{-6}\ mol/L - 4{,}2\ x10^{-11}\ mol/L$$

$$[H_2L^+] = 0{,}0100\ mol/L \Longrightarrow \text{no debemos utilizar aproximaciones sucesivas}$$

11.20 ¿Cuántos mL de KOH 1,00 M se deben añadir a 100 mL de una disolución que contiene 10,0 gramos de hidrocloruro de histidina (histidina·HCl, 191,62 g/mol) para obtener un pH de 9,30?

Respuesta/ 85 mL de KOH 1,00 mol/L

Representamos histidina · HCl como H_2His^+

$$H_3His^{2+} \rightleftharpoons H^+ + H_2His^+ \qquad K_{a1} = \frac{[H^+][H_2His^+]}{[H_3His^{2+}]} = 2\ x10^{-2}$$

$$H_2His^+ \rightleftharpoons H^+ + HHis \qquad K_{a2} = \frac{[H^+][HHis]}{[H_2His^+]} = 9{,}5\ x10^{-7}$$

$$HHis \rightleftharpoons H^+ + His^- \qquad K_{a3} = \frac{[H^+][His^-]}{[HHis]} = 8{,}3\ x10^{-10}$$

$$10{,}0\ g\ histidina \cdot HCl * \frac{1000\ mmol\ histidina \cdot HCl}{191{,}62\ g\ histidina \cdot HCl} = 52{,}2\ mmol\ histidina \cdot HCl$$

Si tenemos "52,2 + x" mmol de KOH

	H_2His^+	+	OH^-	$\longrightarrow$	HHis	+	H_2O
$mmol_{inicial}$	52,2		52,2		---		---
$mmol_{final}$	---		---		52,2		---

	HHis	+	OH^-	$\longrightarrow$	His^-	+	H_2O
$mmol_{inicial}$	52,2		x		---		---
$mmol_{final}$	52,2 - x		---		x		---

$$pH = pK_{a3} + \log\frac{[His^-]}{[HHis]}$$

$$9{,}30 = 9{,}08 + \log\frac{x}{52{,}2 - x}$$

$$x = 33 \text{ mmol KOH}$$

$$\text{mmol}_{\text{totales}} \text{ KOH} = 52{,}2 \text{ mmol} + 33 \text{ mmol} = 85 \text{ mmol}$$

$$\frac{85 \text{ mmol KOH}}{1{,}00 \text{ mmol KOH/mL}} = 85 \text{ mL}$$

11.26 El ácido HA tiene una pK_a = 4,00. Usar las ecuaciones 11.17 y 11.18 para hallar la fracción en la forma HA y la fracción en la forma A^- a pH 5,00.

Respuesta/ α_{HA} = 0,091 y α_{A^-} = 0,91

$$pK_a = 4{,}00 \Longrightarrow K_a = 1{,}0\ x10^{-4}\ mol/L$$

$$pH = 5{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-5}\ mol/L$$

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]} = 1{,}0\ x10^{-4}$$

$$\alpha_{HA} = \frac{[H^+]}{[H^+] + K_a} = \frac{1{,}0\ x10^{-5}}{1{,}0\ x10^{-5} + 1{,}0\ x10^{-4}} = 0{,}091$$

$$\alpha_{A^-} = \frac{K_a}{[H^+] + K_a} = \frac{1{,}0\ x10^{-4}}{1{,}0\ x10^{-5} + 1{,}0\ x10^{-4}} = 0{,}91$$

11.27 Un compuesto dibásico, B, tiene pK_{b1} = 4,00 y pK_{b2} = 6,00. Hallar la fracción de la forma BH_2^{2+} a pH 7,00, usando la ecuación 11.19. Fijarse que K_{a1} y K_{a2} en la ecuación 11.19 son las constantes de disociación ácida de BH_2^{2+} ($K_{a1} = K_w/K_{b2}$ y $K_{a2} = K_w/K_{b1}$)

Respuesta/ $\alpha_{HB_2^{2+}} = 0{,}91$

$$pK_{b2} = 6{,}00 \Longrightarrow K_{b2} = 1{,}0\ x10^{-6} \Longrightarrow K_{a1} = 1{,}0\ x10^{-8}$$

$$pK_{b1} = 4{,}00 \Longrightarrow K_{b1} = 1{,}0\ x10^{-4} \Longrightarrow K_{a2} = 1{,}0\ x10^{-10}$$

$$pH = 7{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-7}\ mol/L$$

$$HB_2^{2+} \rightleftharpoons H^+ + HB^+ \qquad K_{a1} = \frac{[H^+][HB^+]}{[HB_2^{2+}]} = 1{,}0\ x10^{-8}$$

$$HB^+ \rightleftharpoons H^+ + B \qquad K_{a2} = \frac{[H^+][B]}{[HB^+]} = 1{,}0x10^{-10}$$

$$\alpha_{HB_2^{2+}} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha_{HB_2^{2+}} = \frac{(1{,}0\ x10^{-7})^2}{(1{,}0\ x10^{-7})^2 + (1{,}0\ x10^{-7})(1{,}0\ x10^{-8}) + (1{,}0\ x10^{-8})(1{,}0\ x10^{-10})} = 0{,}91$$

11.28 a) ¿Qué fracción de etano-1,2-ditiol hay de cada una de sus formas (H_2A, HA^-, A^{2-}) a pH 8,00? b) ¿Y a pH 10,00?

Respuesta/ a) α_{H_2A} = 0,88, α_{HA^-} = 0,12 y $\alpha_{A^{2-}}$ = 4,5 x10^{-4}
b) α_{H_2A} = 0,050, α_{HA^-} = 0,69 y $\alpha_{A^{2-}}$ = 0,26

$$\text{Representamos etano} - 1{,}2 - \text{ditiol como } H_2A$$

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1{,}4\ x10^{-9}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = 3{,}7\ x10^{-11}$$

a)

$$pH = 8{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-8}\ mol/L$$

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

$$\alpha_{H_2A} = \frac{(1{,}0\ x10^{-8})^2}{(1{,}0\ x10^{-8})^2 + (1{,}0\ x10^{-8})(1{,}4\ x10^{-9}) + (1{,}4\ x10^{-9})(3{,}7\ x10^{-11})} = 0{,}88$$

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

$$\alpha_{HA^-} = \frac{(1{,}4\ x10^{-9})(1{,}0\ x10^{-8})}{(1{,}0\ x10^{-8})^2 + (1{,}0\ x10^{-8})(1{,}4\ x10^{-9}) + (1{,}4\ x10^{-9})(3{,}7\ x10^{-11})} = 0{,}12$$

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

$$\alpha_{A^{2-}} = \frac{(1{,}4\ x10^{-9})(3{,}7\ x10^{-11})}{(1{,}0\ x10^{-8})^2 + (1{,}0\ x10^{-8})(1{,}4\ x10^{-9}) + (1{,}4\ x10^{-9})(3{,}7\ x10^{-11})} = 4{,}5\ x10^{-4}$$

b)

$$\text{pH} = 10{,}00 \Longrightarrow [\text{H}^+] = 1{,}0\ \text{x}10^{-10}\ \text{mol/L}$$

$$\alpha_{\text{H}_2\text{A}} = \frac{(1{,}0\ \text{x}10^{-10})^2}{(1{,}0\ \text{x}10^{-10})^2 + (1{,}0\ \text{x}10^{-10})(1{,}4\ \text{x}10^{-9}) + (1{,}4\ \text{x}10^{-9})(3{,}7\ \text{x}10^{-11})} = 0{,}050$$

$$\alpha_{\text{HA}^-} = \frac{(1{,}4\ \text{x}10^{-9})(1{,}0\ \text{x}10^{-10})}{(1{,}0\ \text{x}10^{-10})^2 + (1{,}0\ \text{x}10^{-10})(1{,}4\ \text{x}10^{-9}) + (1{,}4\ \text{x}10^{-9})(3{,}7\ \text{x}10^{-11})} = 0{,}69$$

$$\alpha_{\text{A}^{2-}} = \frac{(1{,}4\ \text{x}10^{-9})(3{,}7\ \text{x}10^{-11})}{(1{,}0\ \text{x}10^{-10})^2 + (1{,}0\ \text{x}10^{-10})(1{,}4\ \text{x}10^{-9}) + (1{,}4\ \text{x}10^{-9})(3{,}7\ \text{x}10^{-11})} = 0{,}26$$

11.29 Calcular α_{H_2A}, α_{HA^-} y $\alpha_{A^{2-}}$ para el ácido maleico a pH a) 1,00, b) 1,91, c) 6,00, d) 6,33 y e) 10,00.

Respuesta/ a) α_{H_2A} = 0,89, α_{HA^-} = 0,11 y $\alpha_{A^{2-}}$ = 5,1 x10^{-7}
b) α_{H_2A} = 0,49, α_{HA^-} = 0,51 y $\alpha_{A^{2-}}$ = 2,0 x10^{-5}
c) α_{H_2A} = 5,5 x10^{-5}, α_{HA^-} = 0,68 y $\alpha_{A^{2-}}$ = 0,32
d) α_{H_2A} = 1,9 x10^{-5}, α_{HA^-} = 0,50 y $\alpha_{A^{2-}}$ = 0,50
e) α_{H_2A} = 1,7 x10^{-12}, α_{HA^-} = 2,1 x10^{-4} y $\alpha_{A^{2-}}$ = 1,0

Representamos ácido maleico como H_2A

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1{,}23\ x10^{-2}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = 4{,}66\ x10^{-7}$$

a)

$$pH = 1{,}00 \Longrightarrow [H^+] = 0{,}10\ mol/L$$

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

$$\alpha_{H_2A} = \frac{(0{,}10)^2}{(0{,}10)^2 + (0{,}10)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}89$$

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

$$\alpha_{HA^-} = \frac{(1{,}23\ x10^{-2})(0{,}10)}{(0{,}10)^2 + (0{,}10)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}11$$

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

$$\alpha_{A^{2-}} = \frac{(1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}{(0{,}10)^2 + (0{,}10)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 5{,}1\ x10^{-7}$$

b)

$$pH = 1{,}91 \Longrightarrow [H^+] = 0{,}012\ mol/L$$

$$\alpha_{H_2A} = \frac{(0{,}012)^2}{(0{,}012)^2 + (0{,}012)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}49$$

$$\alpha_{HA^-} = \frac{(1{,}23\ x10^{-2})(0{,}012)}{(0{,}012)^2 + (0{,}012)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}51$$

$$\alpha_{A^{2-}} = \frac{(1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}{(0{,}012)^2 + (0{,}012)(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 2{,}0\ x10^{-5}$$

c)

$$pH = 6{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-6}\ mol/L$$

$$\alpha_{H_2A} = \frac{(1{,}0\ x10^{-6})^2}{(1{,}0\ x10^{-6})^2 + (1{,}0\ x10^{-6})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}$$

$$= 5{,}5\ x10^{-5}$$

$$\alpha_{HA^-} = \frac{(1{,}23\ x10^{-2})(1{,}0\ x10^{-6})}{(1{,}0\ x10^{-6})^2 + (1{,}0\ x10^{-6})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}68$$

$$\alpha_{A^{2-}} = \frac{(1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}{(1{,}0\ x10^{-6})^2 + (1{,}0\ x10^{-6})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}32$$

d)

$$pH = 6{,}33 \Longrightarrow [H^+] = 4{,}7\ x10^{-7}\ mol/L$$

$$\alpha_{H_2A} = \frac{(4{,}7\ x10^{-7})^2}{(4{,}7\ x10^{-7})^2 + (4{,}7\ x10^{-7})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}$$

$$= 1{,}9\ x10^{-5}$$

$$\alpha_{HA^-} = \frac{(1{,}23\ x10^{-2})(4{,}7\ x10^{-7})}{(4{,}7\ x10^{-7})^2 + (4{,}7\ x10^{-7})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}50$$

$$\alpha_{A^{2-}} = \frac{(1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}{(4{,}7\ x10^{-7})^2 + (4{,}7\ x10^{-7})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 0{,}50$$

e)

$$pH = 10{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-10}\ mol/L$$

$$\alpha_{H_2A} = \frac{(1{,}0\ x10^{-10})^2}{(1{,}0\ x10^{-10})^2 + (1{,}0\ x10^{-10})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}$$

$$= 1{,}7\ x10^{-12}$$

$$\alpha_{HA^-} = \frac{(1{,}23\ x10^{-2})(1{,}0\ x10^{-10})}{(1{,}0\ x10^{-10})^2 + (1{,}0\ x10^{-10})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}$$

$$= 2{,}1\ x10^{-4}$$

$$\alpha_{A^{2-}} = \frac{(1{,}23\ x10^{-2})(4{,}66\ x10^{-7})}{(1{,}0\ x10^{-10})^2 + (1{,}0\ x10^{-10})(1{,}23\ x10^{-2}) + (1{,}23\ x10^{-2})(4{,}66\ x10^{-7})} = 1{,}0$$

11.31 Una disolución que contiene ácido acético, ácido oxálico, amoniaco y piridina tiene un pH de 9,00. ¿Qué fracción de amoniaco está sin protonar?

Respuesta/ 0,36

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \qquad K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = 5{,}70\ x10^{-10}$$

$$pH = 9{,}00 \Longrightarrow [H^+] = 1{,}0\ x10^{-9}\ mol/L$$

$$\alpha_{NH_3} = \frac{K_a}{[H^+] + K_a} = \frac{5{,}70\ x10^{-10}}{1{,}0\ x10^{-9} + 5{,}70\ x10^{-10}} = 0{,}36$$