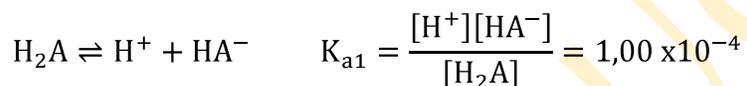


11.4 Considerar el ácido diprótico H_2A de $K_{a1} = 1,00 \times 10^{-4}$ y $K_{a2} = 1,00 \times 10^{-8}$. Hallar el pH y las concentraciones de H_2A , HA^- y A^{2-} de a) H_2A 0,100 M, b) $NaHA$ 0,100 M y c) Na_2A 0,100 M.

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

a)



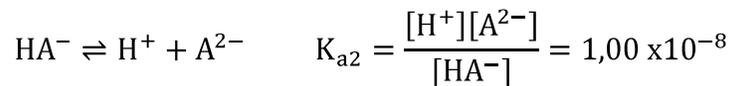
	H_2A	\rightleftharpoons	H^+	+	HA^-
$C_{n_{inicial}}$	0,100		0		0
$C_{n_{final}}$	0,100 - x		x		x

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{(x)(x)}{0,100 - x} = 1,00 \times 10^{-4}$$

$$x = 3,11 \times 10^{-3} \text{ mol/L} = [H^+] = [HA^-]$$

$$pH = 2,507$$

$$[H_2A] = 0,100 - x = 0,100 \text{ mol/L} - 3,11 \times 10^{-3} \text{ mol/L} = 0,097 \text{ mol/L}$$



$$K_{a2} = \frac{(3,11 \times 10^{-3})[A^{2-}]}{(3,11 \times 10^{-3})} = 1,00 \times 10^{-8}$$

$$[A^{2-}] = 1,00 \times 10^{-8} \text{ mol/L}$$

b)

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

$$[H^+] = \sqrt{\frac{(1,00 \times 10^{-4})(1,00 \times 10^{-8})(0,100) + (1,00 \times 10^{-4})(1,01 \times 10^{-14})}{1,00 \times 10^{-4} + 0,100}}$$

$$[H^+] = 1,00 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = 6,000$$

$$H_2A \rightleftharpoons H^+ + HA^- \quad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = 1,00 \times 10^{-4}$$

$$K_{a1} = \frac{(1,00 \times 10^{-6})(0,100)}{[H_2A]} = 1,00 \times 10^{-4}$$

$$[H_2A] = 1,00 \times 10^{-3} \text{ mol/L}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \quad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = 1,00 \times 10^{-8}$$

$$K_{a2} = \frac{(1,00 \times 10^{-6})[A^{2-}]}{(0,100)} = 1,00 \times 10^{-8}$$

$$[A^{2-}] = 1,00 \times 10^{-3} \text{ mol/L}$$

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

$$[HA^-] = 0,100 \text{ mol/L} - 1,00 \times 10^{-3} \text{ mol/L} - 1,00 \times 10^{-3} \text{ mol/L} = 0,098 \text{ mol/L}$$

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

y al hacerlo obtenemos

$$[H^+] = 9,99 \times 10^{-7} \text{ mol/L} \Rightarrow \text{pH} = 6,000$$

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

y al hacerlo obtenemos

$$[H_2A] = 9,79 \times 10^{-4} \text{ mol/L}$$

$$[A^{2-}] = 9,81 \times 10^{-4} \text{ mol/L}$$

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

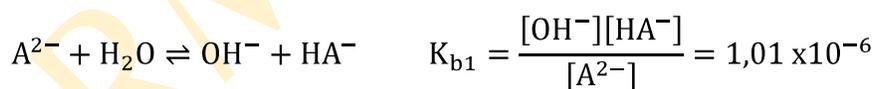
y al hacerlo obtenemos

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

c)

$$K_{a2} = 1,00 \times 10^{-8} \Rightarrow K_{b1} = 1,01 \times 10^{-6}$$

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



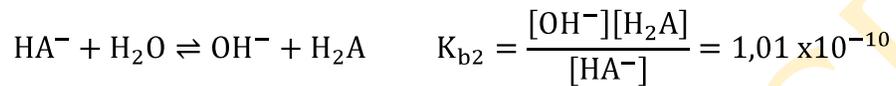
	A^{2-}	+ H_2O	\rightleftharpoons	OH^-	+	HA^-
$C_{n_{inicial}}$	0,100	---		0		0
$C_{n_{final}}$	0,100 - x	---		x		x

$$K_{b1} = \frac{[OH^-][HA^-]}{[A^{2-}]} = \frac{(x)(x)}{0,100 - x} = 1,01 \times 10^{-6}$$

$$x = 3,17 \times 10^{-4} \text{ mol/L} = [\text{OH}^-] = [\text{HA}^-]$$

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

$$[\text{A}^{2-}] = 0,100 - x = 0,100 \text{ mol/L} - 3,17 \times 10^{-4} \text{ mol/L} = 0,100 \text{ mol/L}$$



$$K_{b2} = \frac{(3,17 \times 10^{-4})[\text{H}_2\text{A}]}{(3,17 \times 10^{-4})} = 1,01 \times 10^{-10}$$

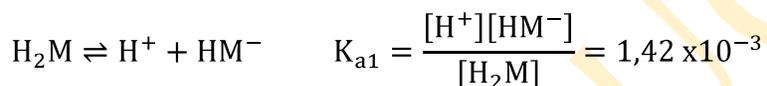
$$[\text{H}_2\text{A}] = 1,01 \times 10^{-10} \text{ mol/L}$$

FARMACIA UCR

11.5 Si al ácido malónico, $\text{CH}_2(\text{CO}_2\text{H})_2$, 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) $\text{pH} = 1,951$, $[\text{H}_2\text{M}] = 0,089 \text{ mol/L}$, $[\text{HM}^-] = 0,0112 \text{ mol/L}$ y $[\text{M}^{2-}] = 2,01 \times 10^{-6} \text{ mol/L}$
 b) $\text{pH} = 4,276$, $[\text{H}_2\text{M}] = 3,47 \times 10^{-3} \text{ mol/L}$, $[\text{HM}^-] = 0,093 \text{ mol/L}$ y $[\text{M}^{2-}] = 3,53 \times 10^{-3} \text{ mol/L}$
 c) $\text{pH} = 9,346$, $[\text{H}_2\text{M}] = 7,11 \times 10^{-12} \text{ mol/L}$, $[\text{HM}^-] = 2,24 \times 10^{-5} \text{ mol/L}$ y $[\text{M}^{2-}] = 0,100 \text{ mol/L}$

a)



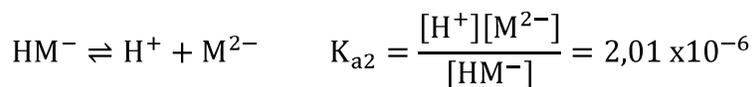
	H_2M	\rightleftharpoons	H^+	+	HM^-
$\text{Cn}_{\text{inicial}}$	0,100		0		0
Cn_{final}	$0,100 - x$		x		x

$$K_{a1} = \frac{[\text{H}^+][\text{HM}^-]}{[\text{H}_2\text{M}]} = \frac{(x)(x)}{0,100 - x} = 1,42 \times 10^{-3}$$

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

$$\text{pH} = 1,951$$

$$[\text{H}_2\text{M}] = 0,100 - x = 0,100 \text{ mol/L} - 0,0112 \text{ mol/L} = 0,089 \text{ mol/L}$$



$$K_{a2} = \frac{(0,0112)[\text{M}^{2-}]}{(0,0112)} = 2,01 \times 10^{-6}$$

$$[M^{2-}] = 2,01 \times 10^{-6} \text{ mol/L}$$

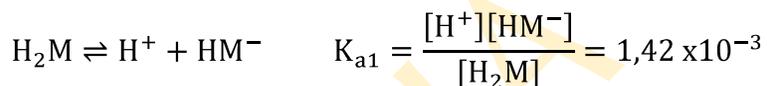
b)

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

$$[H^+] = \sqrt{\frac{(1,42 \times 10^{-3})(2,01 \times 10^{-6})(0,100) + (1,42 \times 10^{-3})(1,01 \times 10^{-14})}{1,42 \times 10^{-3} + 0,100}}$$

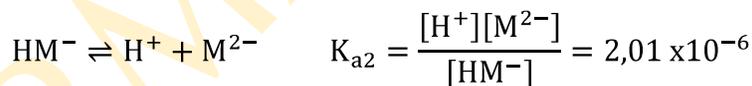
$$[H^+] = 5,30 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = 4,276$$



$$K_{a1} = \frac{(5,30 \times 10^{-5})(0,100)}{[H_2M]} = 1,42 \times 10^{-3}$$

$$[H_2M] = 3,73 \times 10^{-3} \text{ mol/L}$$



$$K_{a2} = \frac{(5,30 \times 10^{-5})[M^{2-}]}{(0,100)} = 2,01 \times 10^{-6}$$

$$[M^{2-}] = 3,79 \times 10^{-3} \text{ mol/L}$$

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

$$[HM^-] = 0,100 \text{ mol/L} - 3,73 \times 10^{-3} \text{ mol/L} - 3,79 \times 10^{-3} \text{ mol/L} = 0,092 \text{ mol/L}$$

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

y al hacerlo obtenemos

$$[H^+] = 5,30 \times 10^{-5} \text{ mol/L} \Rightarrow \text{pH} = 4,276$$

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

y al hacerlo obtenemos

$$[H_2M] = 3,43 \times 10^{-3} \text{ mol/L}$$

$$[M^{2-}] = 3,49 \times 10^{-3} \text{ mol/L}$$

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

y al hacerlo obtenemos

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

si repetimos de nuevo el proceso obtenemos

$$[H_2M] = 3,47 \times 10^{-3} \text{ mol/L}$$

$$[M^{2-}] = 3,53 \times 10^{-3} \text{ mol/L}$$

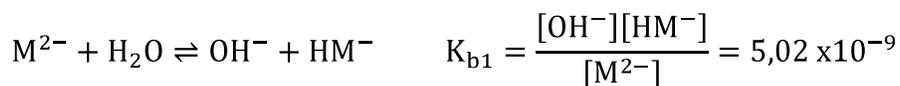
$$[HM^-] = 0,093 \text{ mol/L}$$

∴ hasta aquí es suficiente

c)

$$K_{a2} = 2,01 \times 10^{-6} \Rightarrow K_{b1} = 5,02 \times 10^{-9}$$

$$K_{a1} = 1,42 \times 10^{-3} \Rightarrow K_{b2} = 7,11 \times 10^{-12}$$



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

$$K_{b1} = \frac{[OH^-][HM^-]}{[M^{2-}]} = \frac{(x)(x)}{0,100 - x} = 5,02 \times 10^{-9}$$

$$x = 2,24 \times 10^{-5} \text{ mol/L} = [OH^-] = [HM^-]$$

$$pOH = 4,650 \Rightarrow pH = 9,346$$

$$[M^{2-}] = 0,100 - x = 0,100 \text{ mol/L} - 2,24 \times 10^{-5} \text{ mol/L} = 0,100 \text{ mol/L}$$

$$HM^- + H_2O \rightleftharpoons OH^- + H_2M \quad K_{b2} = \frac{[OH^-][H_2M]}{[HM^-]} = 7,11 \times 10^{-12}$$

$$K_{b2} = \frac{(2,24 \times 10^{-5})[H_2M]}{(2,24 \times 10^{-5})} = 7,11 \times 10^{-12}$$

$$[H_2M] = 7,11 \times 10^{-12} \text{ mol/L}$$

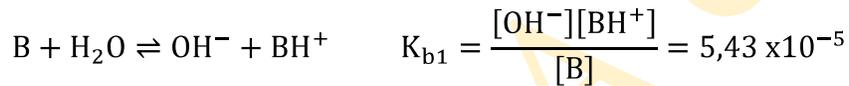
11.6 Calcular el pH de una disolución de piperacina 0,300 M. Calcular la concentración de cada una de las formas de la piperacina en esta disolución.

Respuesta/ pH = 11,599, [B] = 0,296 mol/L, [BH⁺] = 4,01 x10⁻³ mol/L y [BH₂²⁺] = 2,17 x10⁻⁹ mol/L

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

$$K_{a1} = 4,65 \times 10^{-6} \Rightarrow K_{b2} = 2,17 \times 10^{-9}$$

Representamos piperacina como B



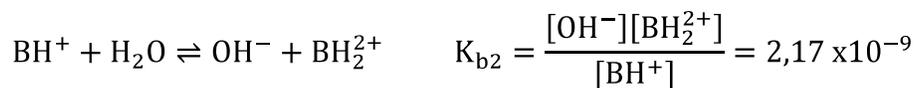
	B	+ H ₂ O	⇌	OH ⁻	+	BH ⁺
Cn _{inicial}	0,300	---		0		0
Cn _{final}	0,300- x	---		x		x

$$K_{b1} = \frac{[OH^-][BH^+]}{[B]} = \frac{(x)(x)}{0,300 - x} = 5,43 \times 10^{-5}$$

$$x = 4,01 \times 10^{-3} \text{ mol/L} = [OH^-] = [BH^+]$$

$$pOH = 2,397 \Rightarrow pH = 11,599$$

$$[B] = 0,300 - x = 0,300 \text{ mol/L} - 4,01 \times 10^{-3} \text{ mol/L} = 0,296 \text{ mol/L}$$



$$K_{b2} = \frac{(4,01 \times 10^{-3})[BH_2^{2+}]}{(4,01 \times 10^{-3})} = 2,17 \times 10^{-9}$$

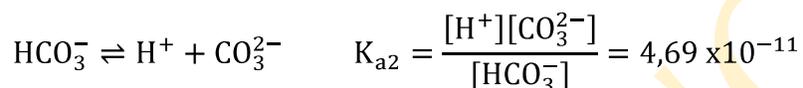
$$[BH_2^{2+}] = 2,17 \times 10^{-9} \text{ mol/L}$$

FARMACIA UCR

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

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



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

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

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

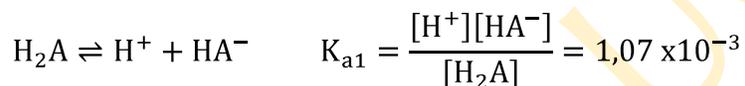
$$\frac{0,279 \text{ mol CO}_3^{2-}}{\text{L}} * \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CO}_3^{2-}} * \frac{105,99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} * 0,100 \text{ L} = 2,96 \text{ g Na}_2\text{CO}_3$$

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 H₂A



Si tenemos "x" mmol de NaOH

	H ₂ A	+	OH ⁻	→	HA ⁻	+	H ₂ O
mmol _{inicial}	0,582		x		---		---
mmol _{final}	0,582 - x		---		x		---

$$\text{pH} = \text{pK}_{a1} + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]}$$

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

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

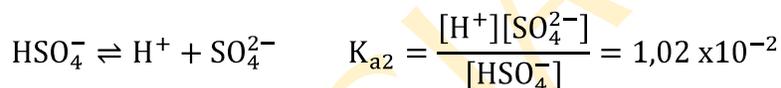
$$\frac{0,449 \text{ mmol KOH}}{0,202 \text{ mmol KOH/mL}} = 2,22 \text{ mL}$$

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 ($= \text{SO}_4^{2-} + \text{HSO}_4^- + \text{H}_2\text{SO}_4$) 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	→	2NaHSO_4
mol _{inicial}	x		y		---
mol _{final}	---		y - x		2x



$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

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

$$x + y = 0,200 \Rightarrow y = 0,200 - x$$

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

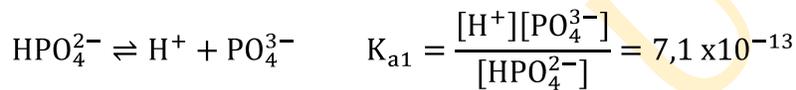
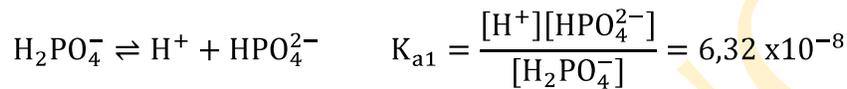
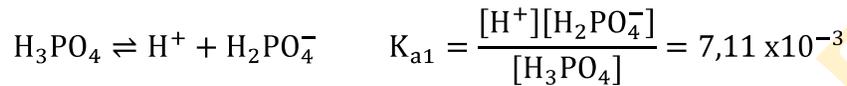
$$x = 0,0134 \text{ mol } \text{H}_2\text{SO}_4 \Rightarrow y = 0,187 \text{ mol } \text{Na}_2\text{SO}_4$$

$$0,0134 \text{ mol } \text{H}_2\text{SO}_4 * \frac{98,07 \text{ g } \text{H}_2\text{SO}_4}{\text{mol } \text{H}_2\text{SO}_4} = 1,31 \text{ g } \text{H}_2\text{SO}_4$$

$$0,187 \text{ mol } \text{Na}_2\text{SO}_4 * \frac{142,04 \text{ g } \text{Na}_2\text{SO}_4}{\text{mol } \text{Na}_2\text{SO}_4} = 26,6 \text{ g } \text{Na}_2\text{SO}_4$$

- 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) $2,78 \times 10^{-3}$
 b) $3,4 \times 10^{-8}$



a)

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

$$[H^+] = \sqrt{\frac{(7,11 \times 10^{-3})(6,32 \times 10^{-8})(0,050) + (7,11 \times 10^{-3})(1,01 \times 10^{-14})}{7,11 \times 10^{-3} + 0,0500}}$$

$$[H^+] = 1,98 \times 10^{-5} \text{ mol/L}$$

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(1,98 \times 10^{-5})[H_2PO_4^-]}{[H_3PO_4]} = 7,11 \times 10^{-3}$$

$$\frac{[H_3PO_4]}{[H_2PO_4^-]} = 2,78 \times 10^{-3}$$

b)

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

$$[H^+] = \sqrt{\frac{(6,32 \times 10^{-8})(7,1 \times 10^{-13})(0,0500) + (6,32 \times 10^{-8})(1,01 \times 10^{-14})}{6,32 \times 10^{-8} + 0,0500}}$$

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

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

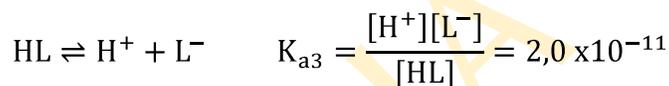
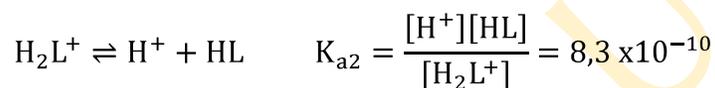
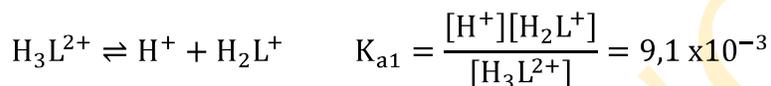
$$\frac{[H_3PO_4]}{[H_2PO_4^-]} = 3,4 \times 10^{-8}$$

FARMACIA UCR

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, $[H_3L^{2+}] = 2,2 \times 10^{-6}$ mol/L, $[H_2L^+] = 0,0100$ mol/L, $[HL] = 4,2 \times 10^{-6}$ mol/L y $[L^-] = 4,2 \times 10^{-11}$ mol/L

Representamos lisina · HCl como H_2L^+

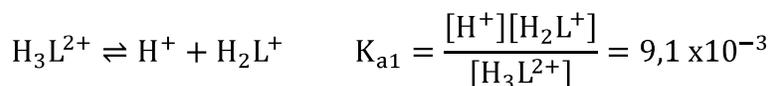


$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[H_2L^+] + K_{a1}K_w}{K_{a1} + [H_2L^+]}} \Rightarrow \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

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

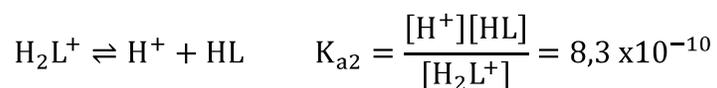
$$[H^+] = 2,0 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = 5,70$$



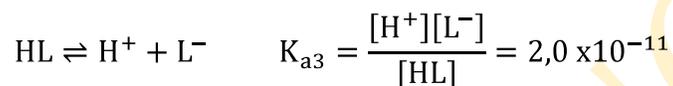
$$K_{a1} = \frac{(2,0 \times 10^{-6})(0,0100)}{[H_3L^{2+}]} = 9,1 \times 10^{-3}$$

$$[H_3L^{2+}] = 2,2 \times 10^{-6} \text{ mol/L}$$



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

$$[\text{HL}] = 4,2 \times 10^{-6} \text{ mol/L}$$



$$K_{a3} = \frac{(2,0 \times 10^{-6})[\text{L}^-]}{4,2 \times 10^{-6}} = 2,0 \times 10^{-11}$$

$$[\text{L}^-] = 4,2 \times 10^{-11} \text{ mol/L}$$

$$[\text{H}_2\text{L}^+] = F - [\text{H}_3\text{L}^{2+}] - [\text{HL}] - [\text{L}^-]$$

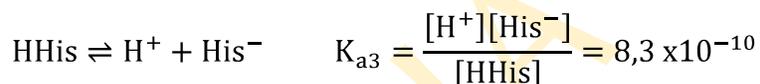
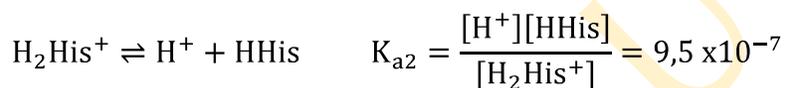
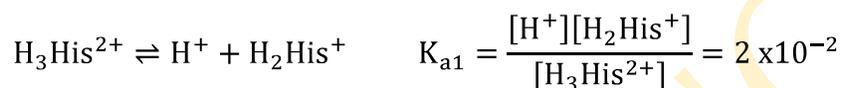
$$[\text{H}_2\text{L}^+] = 0,0100 \text{ mol/L} - 2,2 \times 10^{-6} \text{ mol/L} - 4,2 \times 10^{-6} \text{ mol/L} - 4,2 \times 10^{-11} \text{ mol/L}$$

$$[\text{H}_2\text{L}^+] = 0,0100 \text{ mol/L} \Rightarrow \text{no debemos utilizar aproximaciones sucesivas}$$

11.20 ¿Cuántos mL de KOH 1,00 M se deben añadir a 100 mL de una disolución que contiene 10,0 gramos de hidrocloreto 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^+



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

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

	H_2His^+	+	OH^-	→	HHis	+	H_2O
mmol _{inicial}	52,2		52,2		---		---
mmol _{final}	---		---		52,2		---

	HHis	+	OH^-	→	His^-	+	H_2O
mmol _{inicial}	52,2		x		---		---
mmol _{final}	52,2 - x		---		x		---

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

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

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

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

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

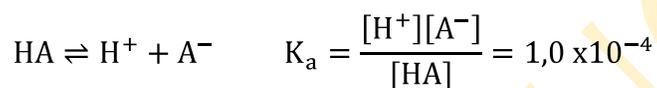
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11.26 El ácido HA tiene una $pK_a = 4,00$. Usar las ecuaciones 11.17 y 11.18 para hallar la fracción en la forma HA y la fracción en la forma A^- a pH 5,00.

Respuesta/ $\alpha_{HA} = 0,091$ y $\alpha_{A^-} = 0,91$

$$pK_a = 4,00 \Rightarrow K_a = 1,0 \times 10^{-4} \text{ mol/L}$$

$$pH = 5,00 \Rightarrow [H^+] = 1,0 \times 10^{-5} \text{ mol/L}$$



$$\alpha_{HA} = \frac{[H^+]}{[H^+] + K_a} = \frac{1,0 \times 10^{-5}}{1,0 \times 10^{-5} + 1,0 \times 10^{-4}} = 0,091$$

$$\alpha_{A^-} = \frac{K_a}{[H^+] + K_a} = \frac{1,0 \times 10^{-4}}{1,0 \times 10^{-5} + 1,0 \times 10^{-4}} = 0,91$$

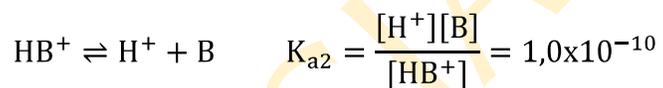
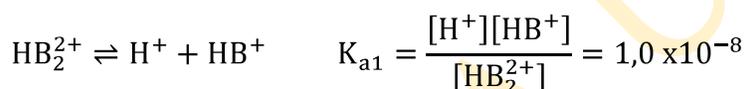
11.27 Un compuesto dibásico, B, tiene $pK_{b1} = 4,00$ y $pK_{b2} = 6,00$. Hallar la fracción de la forma BH_2^{2+} a pH 7,00, usando la ecuación 11.19. Fijarse que K_{a1} y K_{a2} en la ecuación 11.19 son las constantes de disociación ácida de BH_2^{2+} ($K_{a1} = K_w/K_{b2}$ y $K_{a2} = K_w/K_{b1}$)

Respuesta/ $\alpha_{BH_2^{2+}} = 0,91$

$$pK_{b2} = 6,00 \Rightarrow K_{b2} = 1,0 \times 10^{-6} \Rightarrow K_{a1} = 1,0 \times 10^{-8}$$

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

$$pH = 7,00 \Rightarrow [H^+] = 1,0 \times 10^{-7} \text{ mol/L}$$



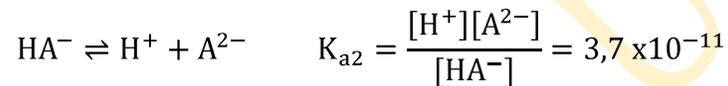
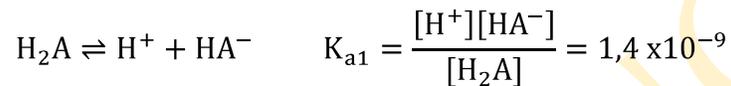
$$\alpha_{BH_2^{2+}} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha_{BH_2^{2+}} = \frac{(1,0 \times 10^{-7})^2}{(1,0 \times 10^{-7})^2 + (1,0 \times 10^{-7})(1,0 \times 10^{-8}) + (1,0 \times 10^{-8})(1,0 \times 10^{-10})} = 0,91$$

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) $\alpha_{H_2A} = 0,88$, $\alpha_{HA^-} = 0,12$ y $\alpha_{A^{2-}} = 4,5 \times 10^{-4}$
 b) $\alpha_{H_2A} = 0,050$, $\alpha_{HA^-} = 0,69$ y $\alpha_{A^{2-}} = 0,26$

Representamos etano – 1,2 – ditiol como H_2A



a)

$$pH = 8,00 \Rightarrow [H^+] = 1,0 \times 10^{-8} \text{ mol/L}$$

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

$$\alpha_{H_2A} = \frac{(1,0 \times 10^{-8})^2}{(1,0 \times 10^{-8})^2 + (1,0 \times 10^{-8})(1,4 \times 10^{-9}) + (1,4 \times 10^{-9})(3,7 \times 10^{-11})} = 0,88$$

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

$$\alpha_{HA^-} = \frac{(1,4 \times 10^{-9})(1,0 \times 10^{-8})}{(1,0 \times 10^{-8})^2 + (1,0 \times 10^{-8})(1,4 \times 10^{-9}) + (1,4 \times 10^{-9})(3,7 \times 10^{-11})} = 0,12$$

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

$$\alpha_{A^{2-}} = \frac{(1,4 \times 10^{-9})(3,7 \times 10^{-11})}{(1,0 \times 10^{-8})^2 + (1,0 \times 10^{-8})(1,4 \times 10^{-9}) + (1,4 \times 10^{-9})(3,7 \times 10^{-11})} = 4,5 \times 10^{-4}$$

b)

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

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

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

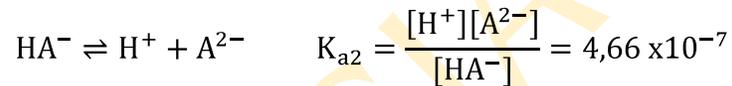
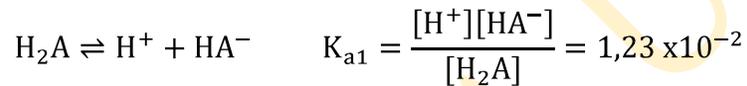
$$\alpha_{\text{A}^{2-}} = \frac{(1,4 \times 10^{-9})(3,7 \times 10^{-11})}{(1,0 \times 10^{-10})^2 + (1,0 \times 10^{-10})(1,4 \times 10^{-9}) + (1,4 \times 10^{-9})(3,7 \times 10^{-11})} = 0,26$$

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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) $\alpha_{H_2A} = 0,89$, $\alpha_{HA^-} = 0,11$ y $\alpha_{A^{2-}} = 5,1 \times 10^{-7}$
 b) $\alpha_{H_2A} = 0,49$, $\alpha_{HA^-} = 0,51$ y $\alpha_{A^{2-}} = 2,0 \times 10^{-5}$
 c) $\alpha_{H_2A} = 5,5 \times 10^{-5}$, $\alpha_{HA^-} = 0,68$ y $\alpha_{A^{2-}} = 0,32$
 d) $\alpha_{H_2A} = 1,9 \times 10^{-5}$, $\alpha_{HA^-} = 0,50$ y $\alpha_{A^{2-}} = 0,50$
 e) $\alpha_{H_2A} = 1,7 \times 10^{-12}$, $\alpha_{HA^-} = 2,1 \times 10^{-4}$ y $\alpha_{A^{2-}} = 1,0$

Representamos ácido maleico como H_2A



a)

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

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

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

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

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

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

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

b)

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

$$\alpha_{\text{H}_2\text{A}} = \frac{(0,012)^2}{(0,012)^2 + (0,012)(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,49$$

$$\alpha_{\text{HA}^-} = \frac{(1,23 \times 10^{-2})(0,012)}{(0,012)^2 + (0,012)(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,51$$

$$\alpha_{A^{2-}} = \frac{(1,23 \times 10^{-2})(4,66 \times 10^{-7})}{(0,012)^2 + (0,012)(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 2,0 \times 10^{-5}$$

c)

$$\text{pH} = 6,00 \Rightarrow [\text{H}^+] = 1,0 \times 10^{-6} \text{ mol/L}$$

$$\alpha_{\text{H}_2\text{A}} = \frac{(1,0 \times 10^{-6})^2}{(1,0 \times 10^{-6})^2 + (1,0 \times 10^{-6})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 5,5 \times 10^{-5}$$

$$\alpha_{\text{HA}^-} = \frac{(1,23 \times 10^{-2})(1,0 \times 10^{-6})}{(1,0 \times 10^{-6})^2 + (1,0 \times 10^{-6})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,68$$

$$\alpha_{A^{2-}} = \frac{(1,23 \times 10^{-2})(4,66 \times 10^{-7})}{(1,0 \times 10^{-6})^2 + (1,0 \times 10^{-6})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,32$$

d)

$$\text{pH} = 6,33 \Rightarrow [\text{H}^+] = 4,7 \times 10^{-7} \text{ mol/L}$$

$$\alpha_{\text{H}_2\text{A}} = \frac{(4,7 \times 10^{-7})^2}{(4,7 \times 10^{-7})^2 + (4,7 \times 10^{-7})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 1,9 \times 10^{-5}$$

$$\alpha_{\text{HA}^-} = \frac{(1,23 \times 10^{-2})(4,7 \times 10^{-7})}{(4,7 \times 10^{-7})^2 + (4,7 \times 10^{-7})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,50$$

$$\alpha_{\text{A}^{2-}} = \frac{(1,23 \times 10^{-2})(4,66 \times 10^{-7})}{(4,7 \times 10^{-7})^2 + (4,7 \times 10^{-7})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} = 0,50$$

e)

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

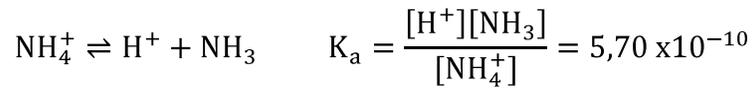
$$\begin{aligned} \alpha_{\text{H}_2\text{A}} &= \frac{(1,0 \times 10^{-10})^2}{(1,0 \times 10^{-10})^2 + (1,0 \times 10^{-10})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} \\ &= 1,7 \times 10^{-12} \end{aligned}$$

$$\begin{aligned} \alpha_{\text{HA}^-} &= \frac{(1,23 \times 10^{-2})(1,0 \times 10^{-10})}{(1,0 \times 10^{-10})^2 + (1,0 \times 10^{-10})(1,23 \times 10^{-2}) + (1,23 \times 10^{-2})(4,66 \times 10^{-7})} \\ &= 2,1 \times 10^{-4} \end{aligned}$$

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

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

Respuesta/ 0,36



$$\text{pH} = 9,00 \Rightarrow [\text{H}^+] = 1,0 \times 10^{-9} \text{ mol/L}$$

$$\alpha_{\text{NH}_3} = \frac{K_a}{[\text{H}^+] + K_a} = \frac{5,70 \times 10^{-10}}{1,0 \times 10^{-9} + 5,70 \times 10^{-10}} = 0,36$$