Soluciones amortiguadoras de pH (*Buffer*)

Unidad-1
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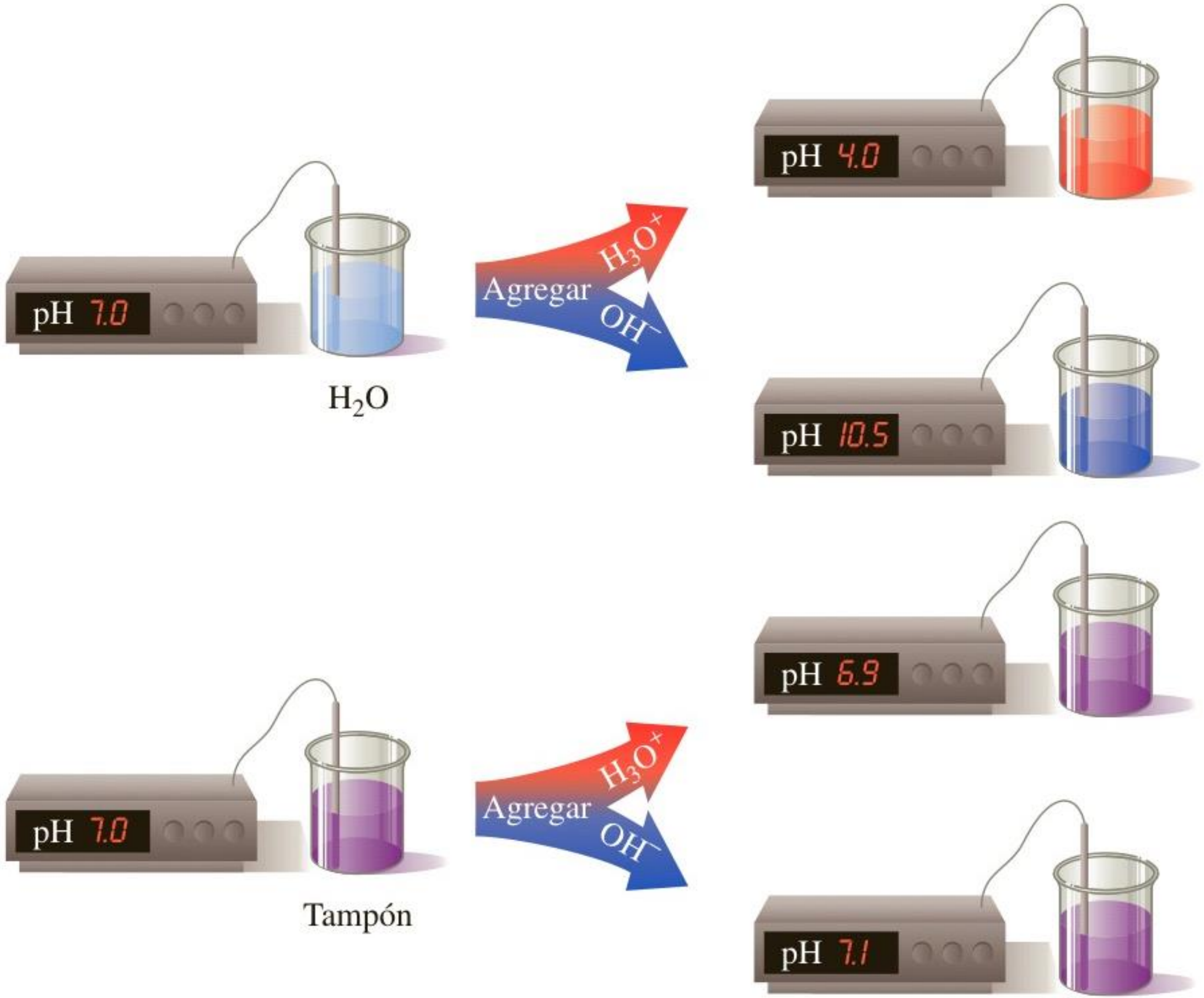
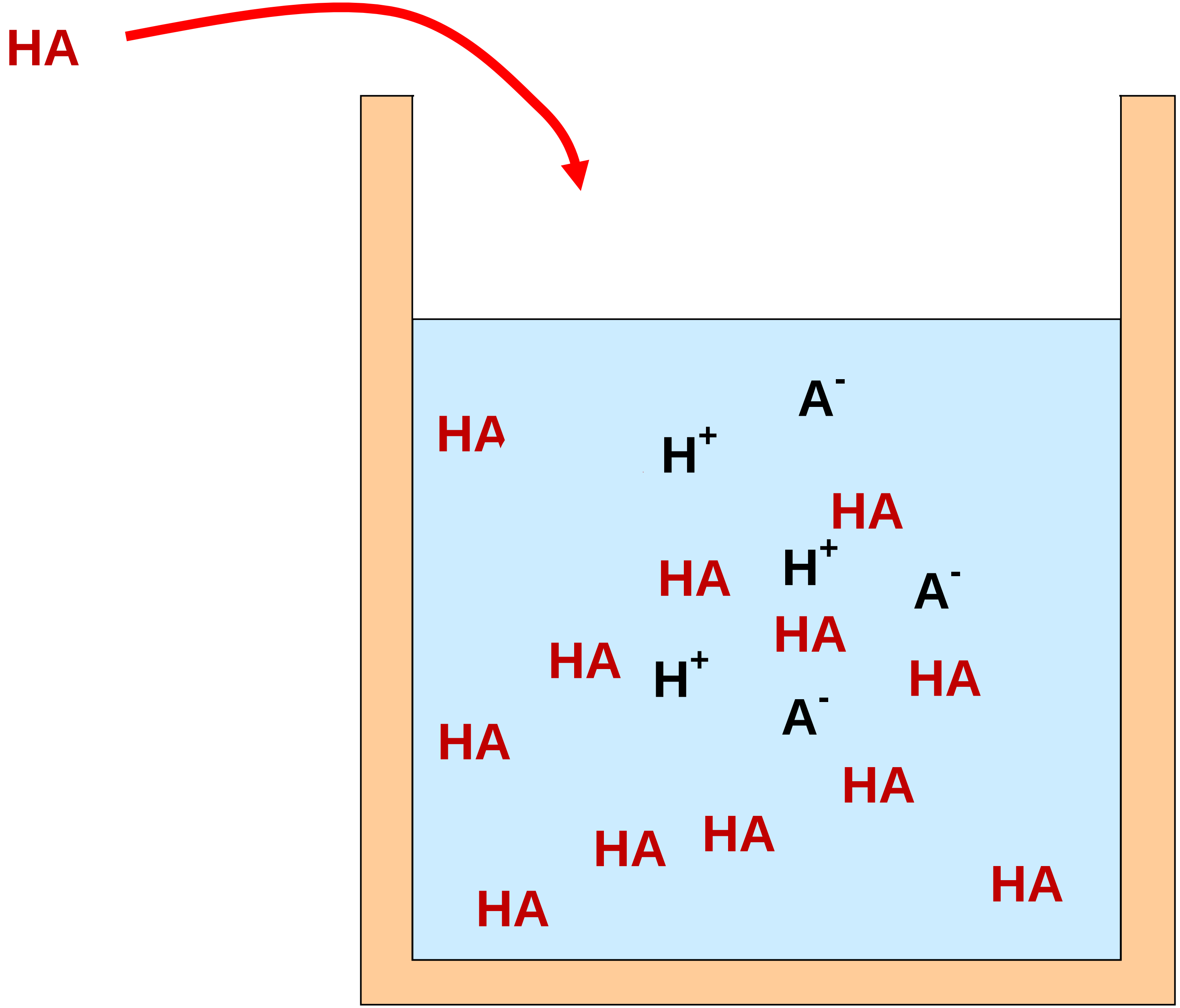

pH 7.0
H₂O
Agregar
H_3O^+
OH^-
pH 4.0
pH 10.5
pH 7.0
Tampón
Agregar
H_3O^+
OH^-
pH 6.9
pH 7.1

¿Cómo funciona una solución amortiguadora de pH?

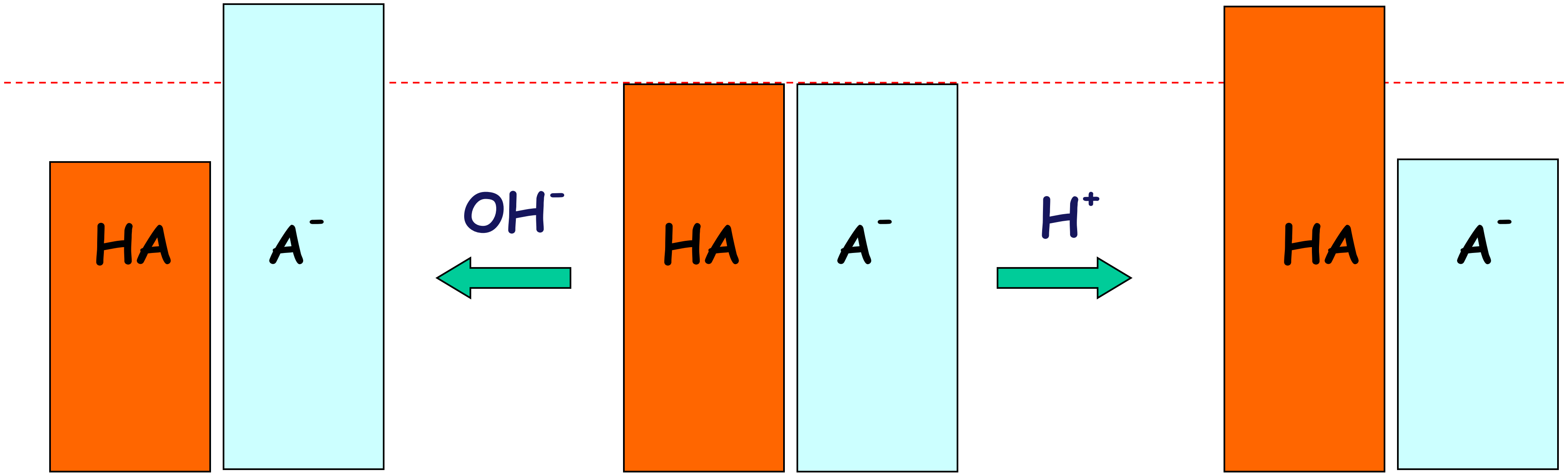
$$HA_{(ac)} \rightleftharpoons H^{+}_{(ac)} + A^{-}_{(ac)}$$

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

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


HA
HA
H+
A-
HA
HA
H+
A-
HA
HA
H+
HA
A-
HA
HA
HA
HA
HA
HA

$$HA_{(ac)} \rightleftharpoons H^+_{(ac)} + A^-_{(ac)}$$



De acuerdo con el principio de Le Chatelier, este sistema en equilibrio exhibe la notable propiedad de mantener la concentración de iones de hidrógeno ([H+]) constante, incluso cuando se le adiciona una base o un ácido

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

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

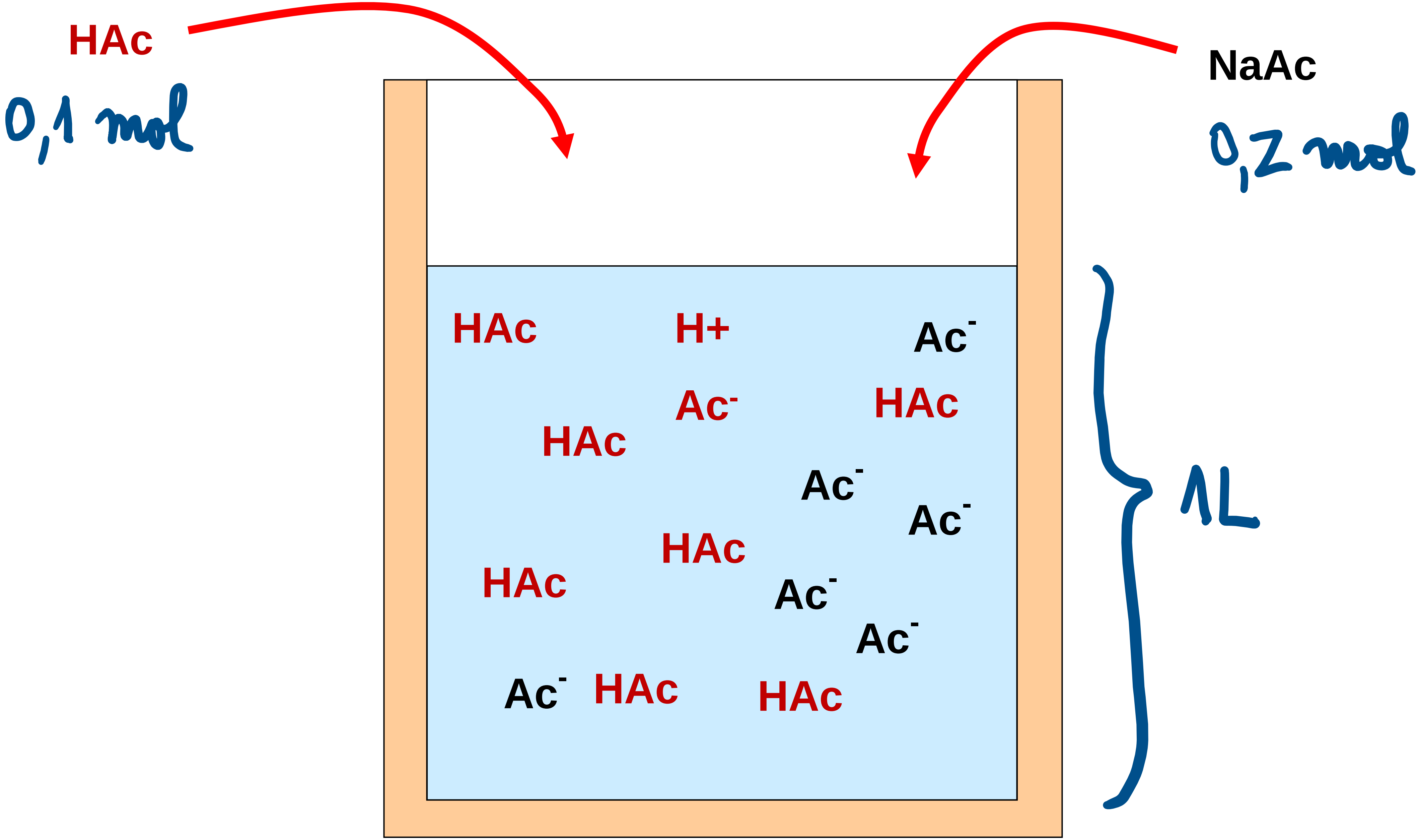
$$\Downarrow$$

$$\boxed{pH = pK_a + \log \frac{[A^-]}{[HA]}}$$

Ecuación de Henderson-Hasselbalch

¿Qué pH se obtiene al mezclar HAc 0,1 M y NaAc 0,2 M? datos: K_a=1,7 x 10^{-5} ; pK_a= 4,7

Nota: Se debe considerar que el ácido acético está muy poco disociado y el acetato de sodio se encuentra completamente disociado. Recordar que el acetato es un electrolito fuerte.


HAc
0,1 mol
NaAc
0,2 mol
HAc
H+
Ac-
Ac-
HAc
HAc
Ac-
Ac-
HAc
HAc
Ac-
Ac-
Ac-
HAc
HAc
1L

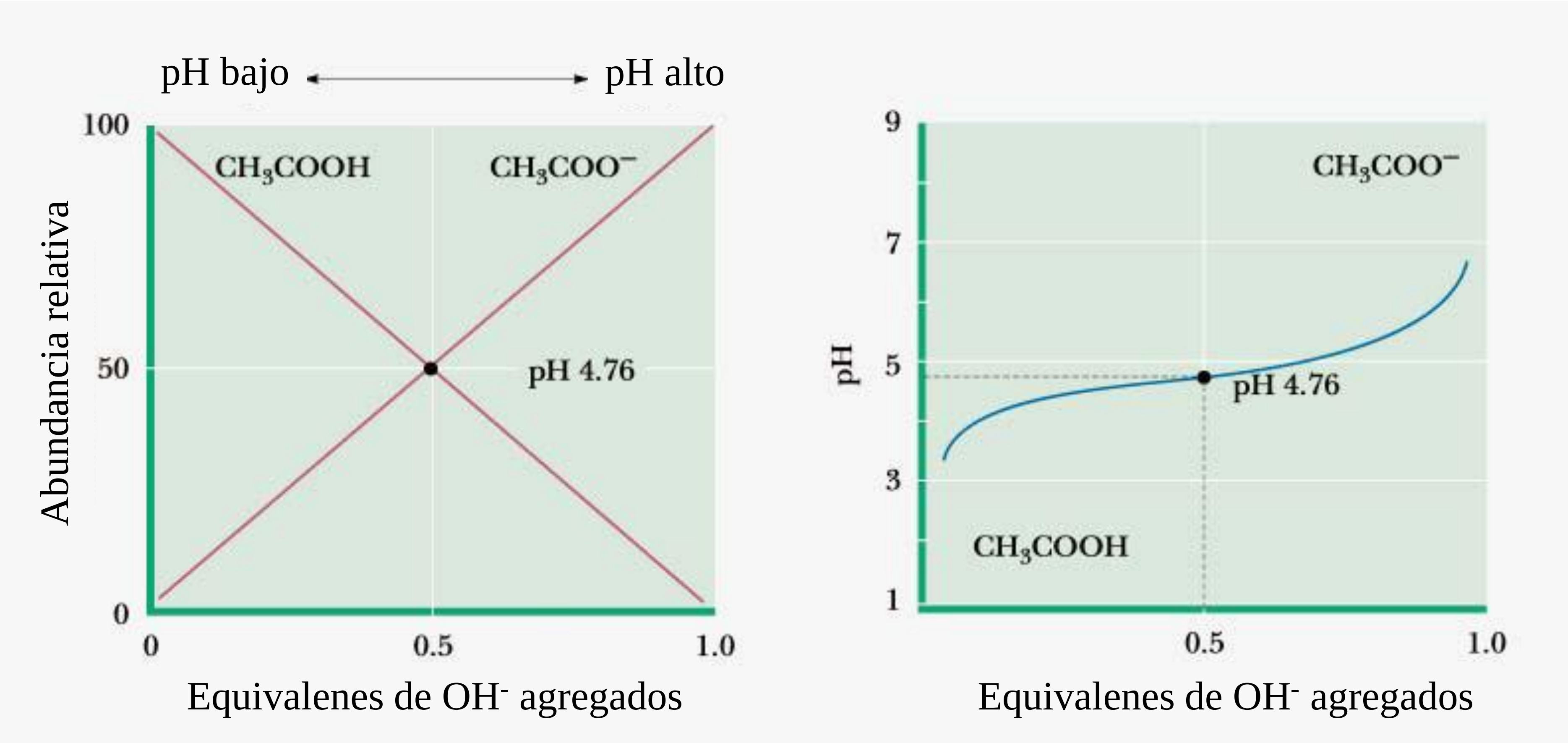
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = 4{,}7 + \log \frac{0{,}2 \text{ (acetato)}}{0{,}1 \text{ (ác. acético)}}$$

$$pH = 4{,}7 + \log 2$$

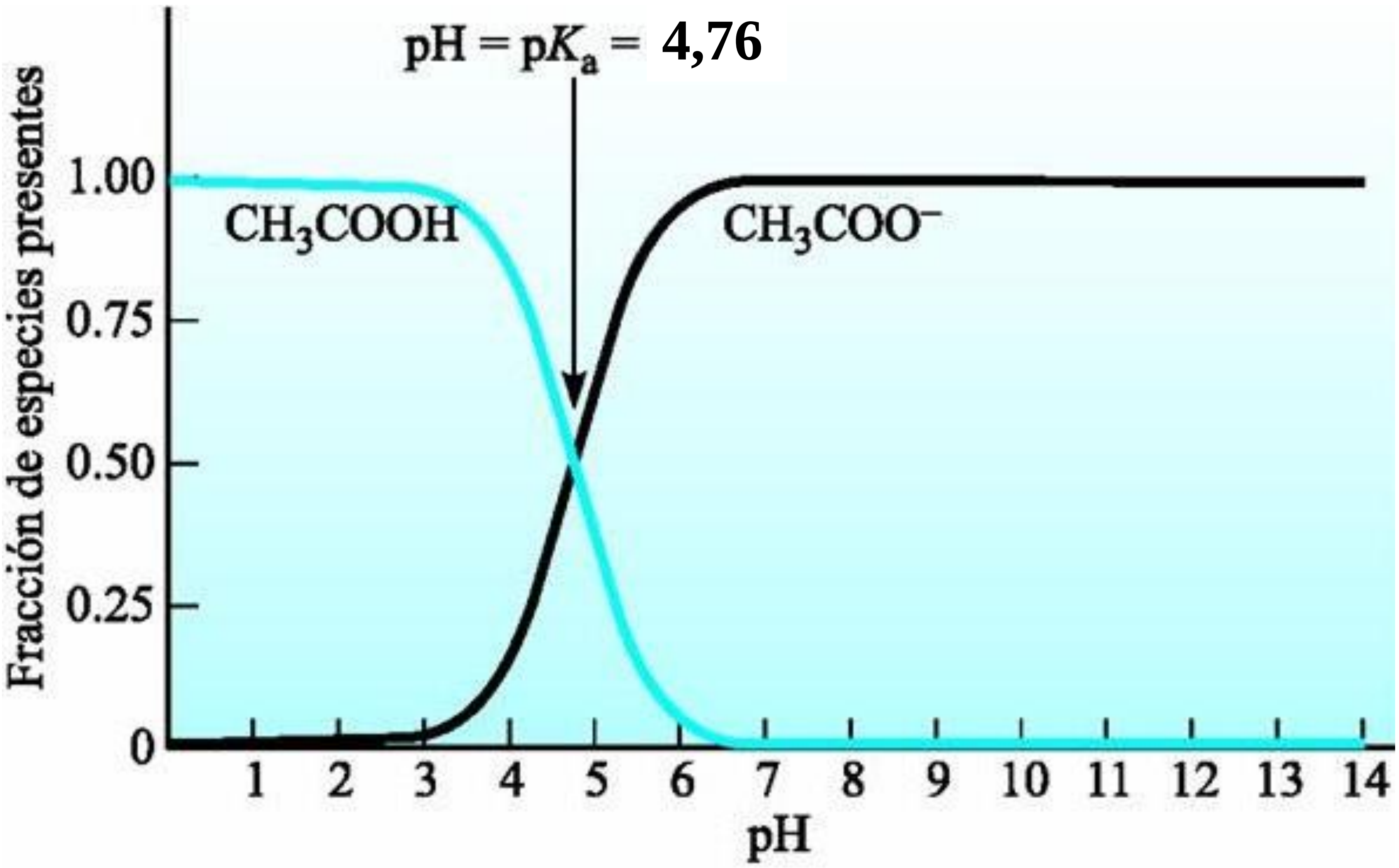
$$pH = 5$$

Nota: Este sistema funciona como “buffer” o solución amortiguadora a pH 5,0



Nota: El ácido acético se encuentra 50% disociado a pH 4,76 que corresponde al valor de su ***pKa***.

$$pH = pK_a + \log \frac{[Ac^-]}{[HAc]}$$


pH = pK_a = 4,76
1.00
0.75
0.50
0.25
0
Fracción de especies presentes
CH_3COOH
CH_3COO^-
1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH

El CO_2 disuelto en agua establece un equilibrio acido-base

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$K_{a1} = 4,3 \times 10^{-7}$

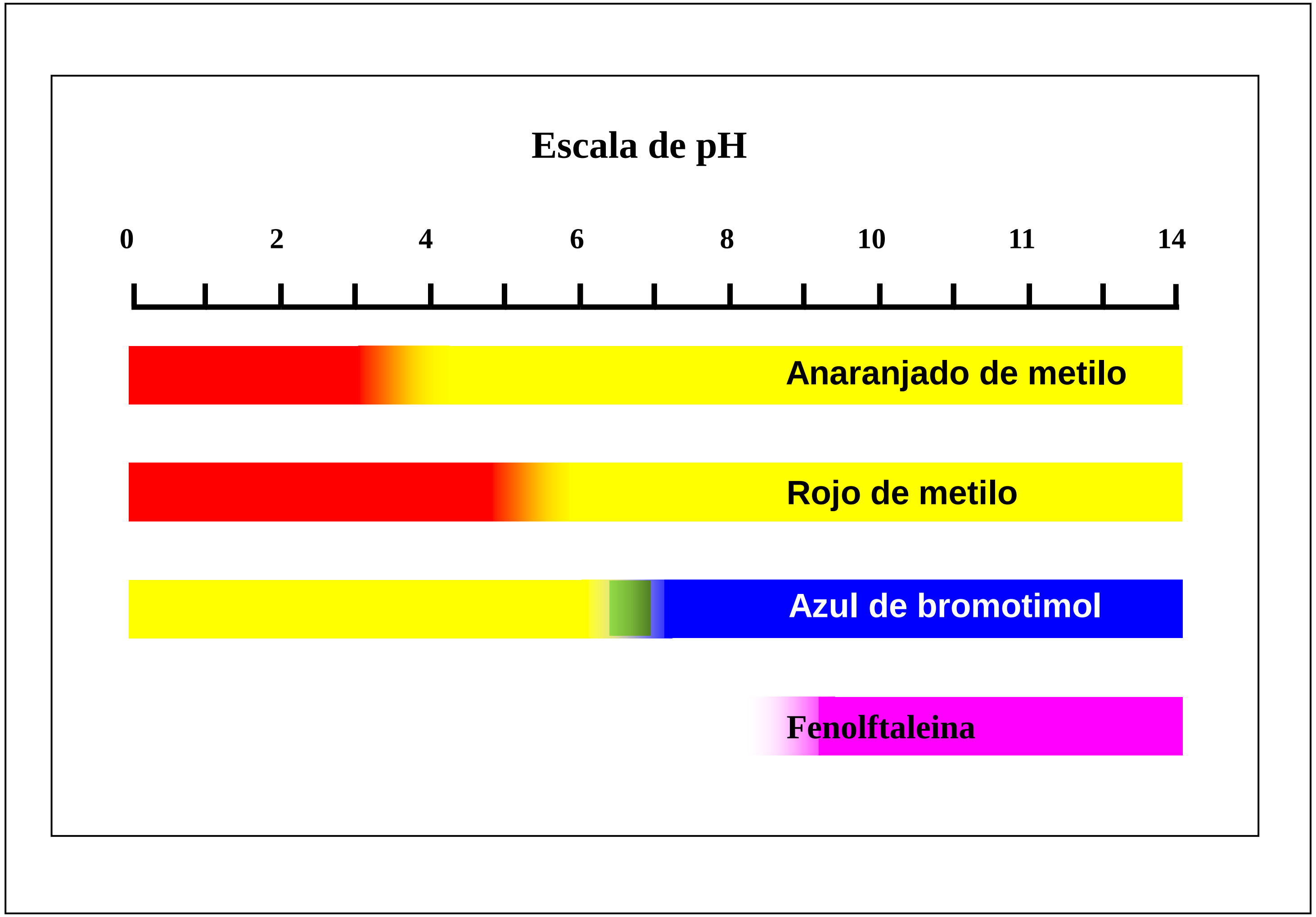
$pK_{a1} = 6,4$

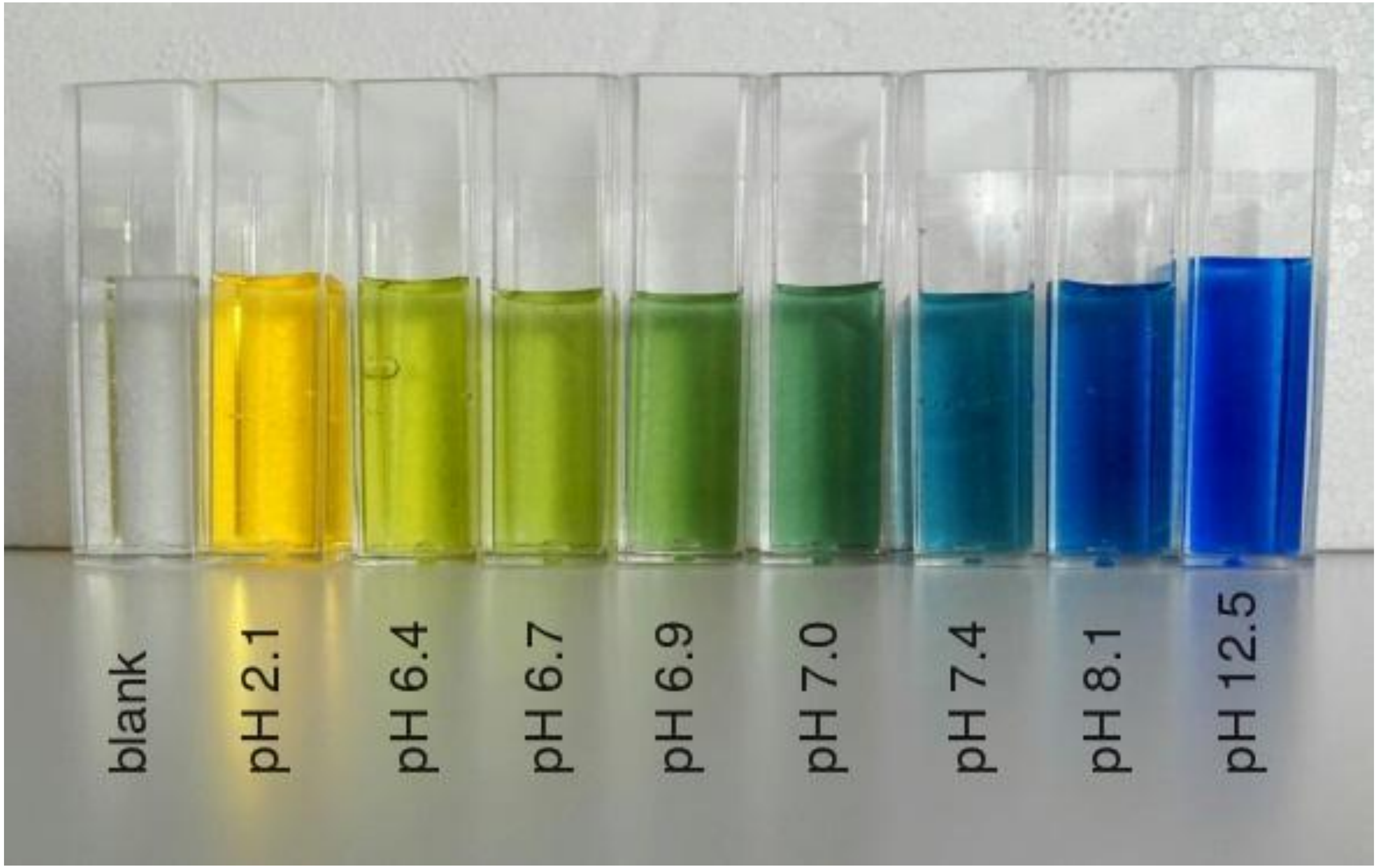
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$$

$K_{a2} = 5,6 \times 10^{-11}$

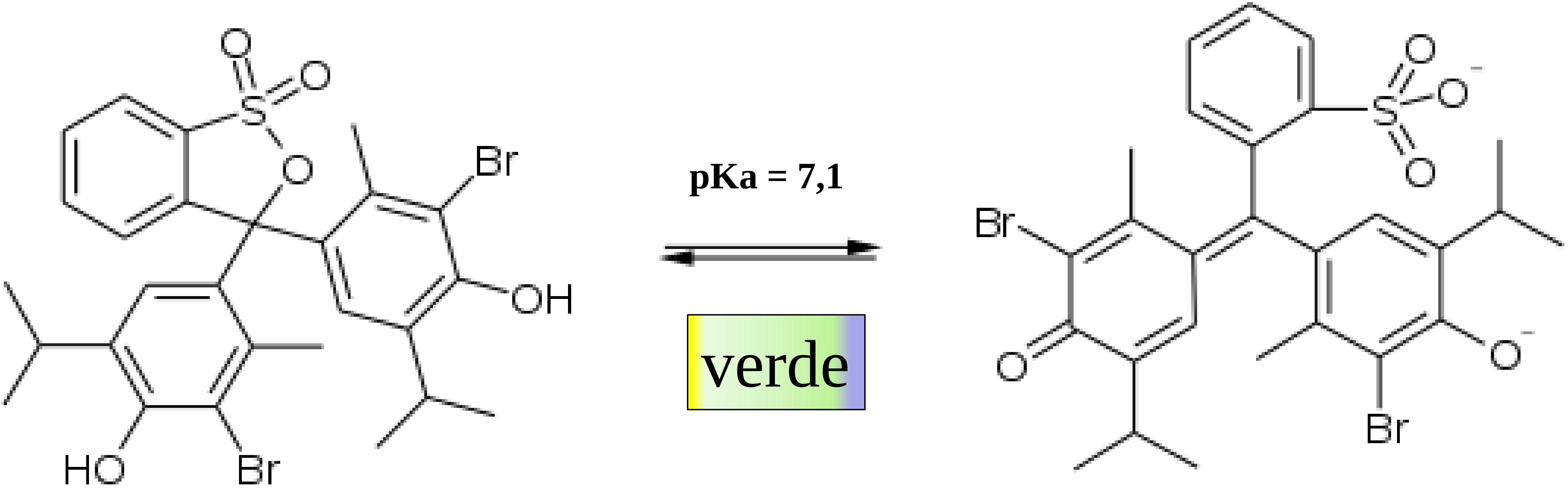
$pK_{a2} = 10,2$

INDICADORES DE pH




blank
pH 2.1
pH 6.4
pH 6.7
pH 6.9
pH 7.0
pH 7.4
pH 8.1
pH 12.5

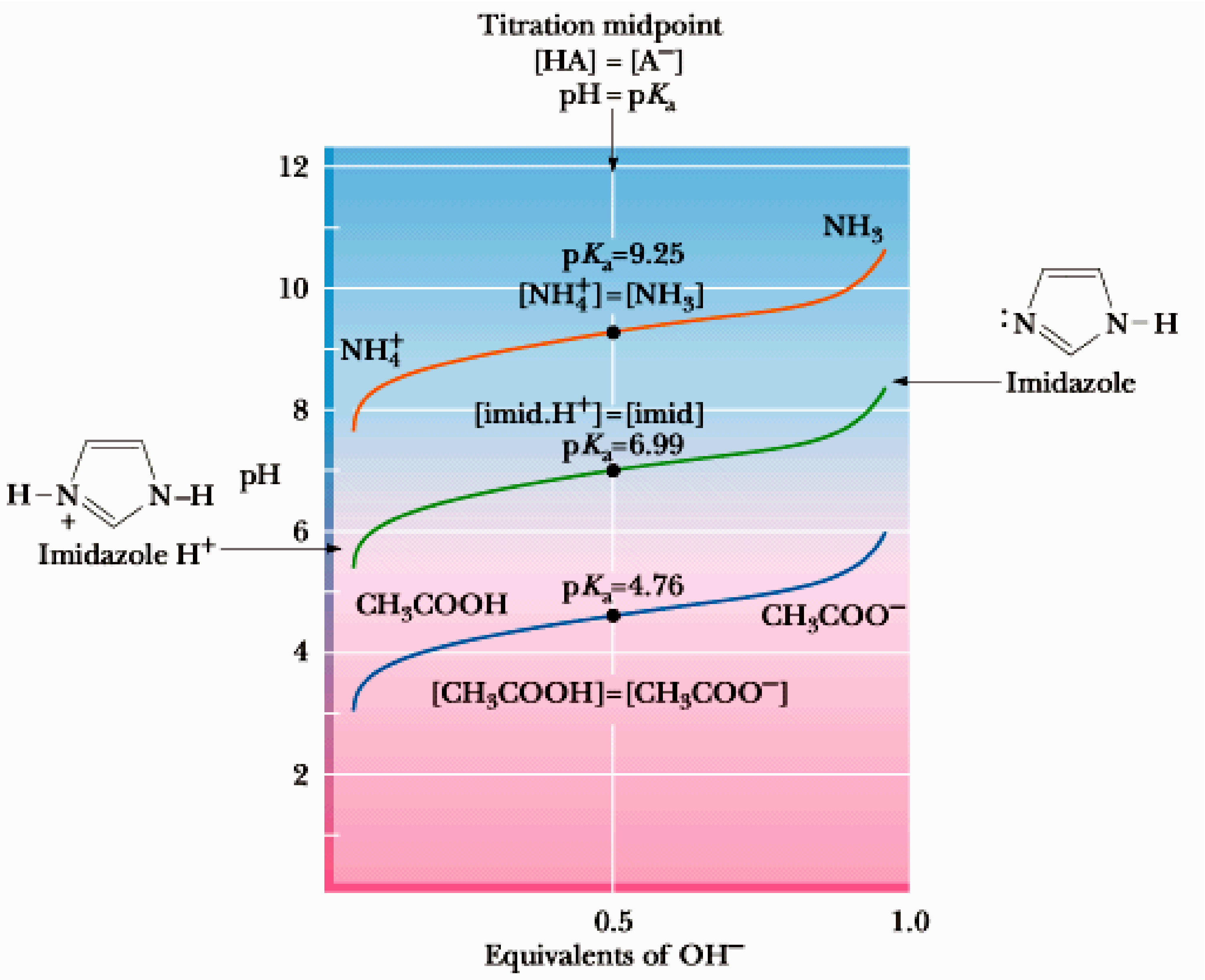
Azul de bromotimol, un indicador de pH



Color amarillo

Color azul

Carbon Dioxide Behaves as an Acid in Water



Titration midpoint
[HA] = [A⁻]
pH = pKa
12
10
8
6
4
2
pH
NH3
pKa=9.25
[NH4+]=[NH3]
NH4+
[imid.H+]=[imid]
pKa=6.99
Imidazole
Imidazole H+
CH3COOH
pKa=4.76
CH3COO⁻
[CH3COOH]=[CH3COO⁻]
0.5
1.0
Equivalents of OH⁻

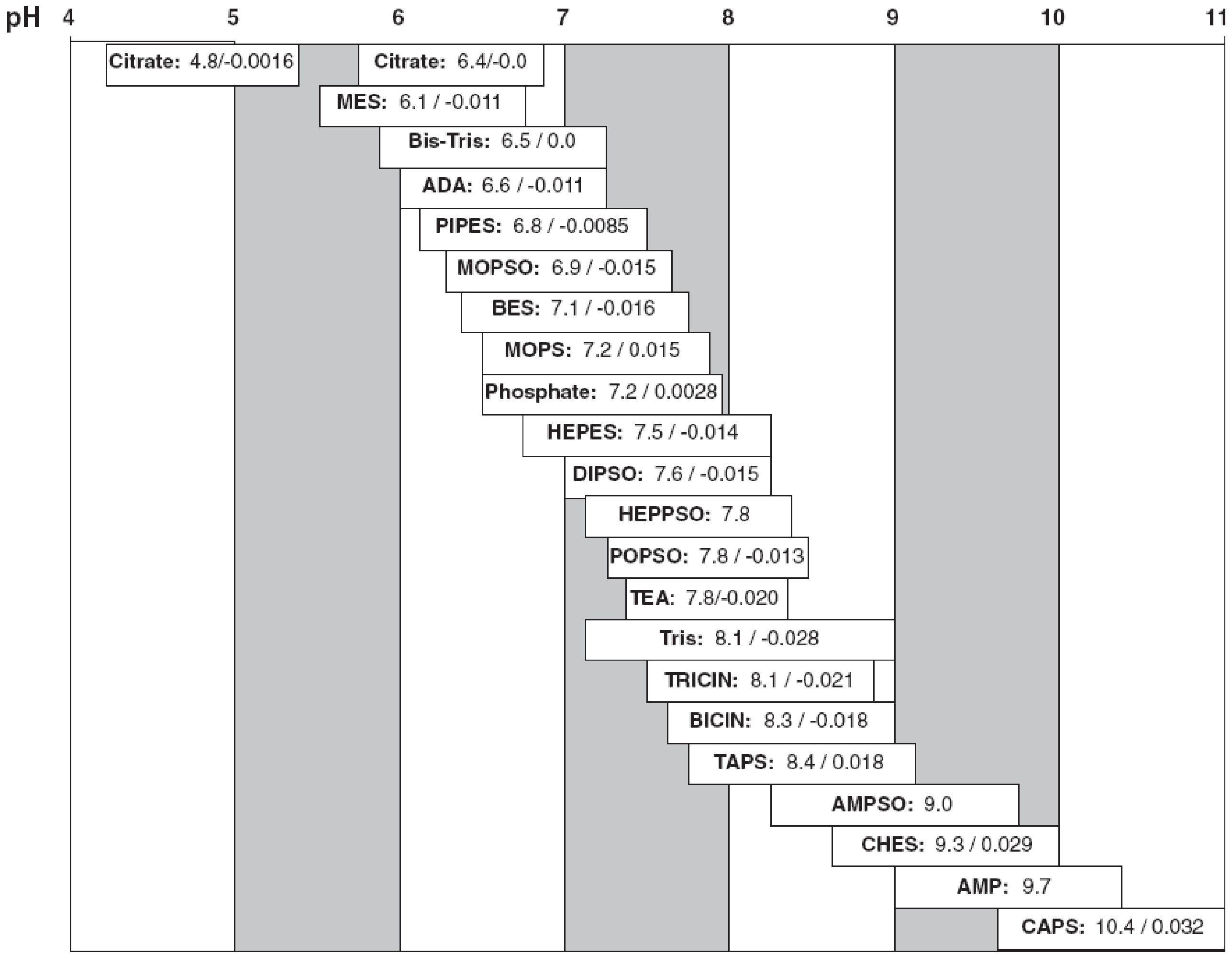
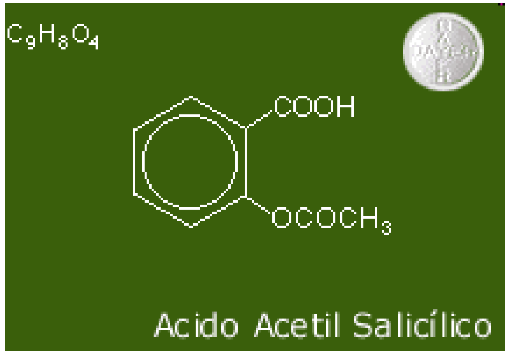


Figure 1.1. Working range, pKa, and temperature dependence of buffers. The numbers behind the buffer names are pKa and its temperature dependence (change of pKa per °C). **MES**: 2-(N-morpholino)-ethanesulfonic acid; **Bis-Tris**: [bis(2-hydroxyethyl)imino]Tris(hydroxymethyl)methane; **ADA**: N-(2 acetamidoimino)diacetic acid; **PIPES**: piperazine-N, N-bis(2-ethane sulfonic acid); **MOPSO**: 3-(N-morpholino)-2-hydroxy propanesulfonic acid; **BES**: N,N-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid; **MOPS**: 3-(N-morpholino) propanesulfonic acid; **HEPES**: N-2-hydroxyethylpiperazine-N-2-ethanesulfonic acid; **DIPSO**: 3-[N-bis(hydroxyethyl)amino]-2-hydroxypropanesulfonic acid; **HEPPSO**: N-(2-hydroxyethyl) piperazine N-(2-hydroxypropanesulfonic acid); **POPSO**: piperazine-N,N-bis(2-hydroxypropanesulfonic acid); **TEA**: triethanolamine; **TRIS**: Tris(hydroxymethyl)aminomethane; **TRICIN**: N-[Tris(hydroxymethyl) methyl]glycine; **BICIN**: N, N-bis(2-hydroxyethyl)glycine; **TAPS**: 3-{[Tris(hydroxymethyl)methyl]amino}propanesulfonic acid; **AMPSO**: 3-[(1,1-dimethyl-2-hydroxy-ethyl)amino]-2-hydroxypropanesulfonic acid; **CHES**: cyclohexylaminoethanesulfonic acid; **AMP**: 3-aminopropanesulfonic acid; **CAPS**: 3-(cyclohexylamino)propanesulfonic acid.

$$pKa - pH = \log([HA]/[A-])$$

Ejemplo:
ác. acetilsalicílico pKa 3,5



a) pH 1,5 (estómago en ayunas)

$$3{,}5 – 1{,}5 = 2 = \log([HA]/[A-])$$

100 no ionizada/1 ionizada

b) pH 2,5 (estómago con alimentos)

$$3{,}5 – 2{,}5 = 1 = \log([HA]/[A-])$$

10 no ionizada/ 1 ionizada

$$pKa - pH = \log ([HA]/ [A-])$$

Ejemplo:
ác. acetilsalicílico pKa 3,5

c) pH 3,5 (estómago con alimentos)

$$3{,}5 – 3{,}5 = 0 = \log ([HA]/ [A-])$$

1 no ionizada/1 ionizada

d) pH 6,5 (duodeno)

$$3{,}5 – 6{,}5 = -3 = \log ([HA]/ [A-])$$

1 no ionizada/ 1000 ionizada

La disociación del H_3PO_4

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$K_{a1} = 7,5 \times 10^{-3}$

$pK_{a1} = 2,1$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$$

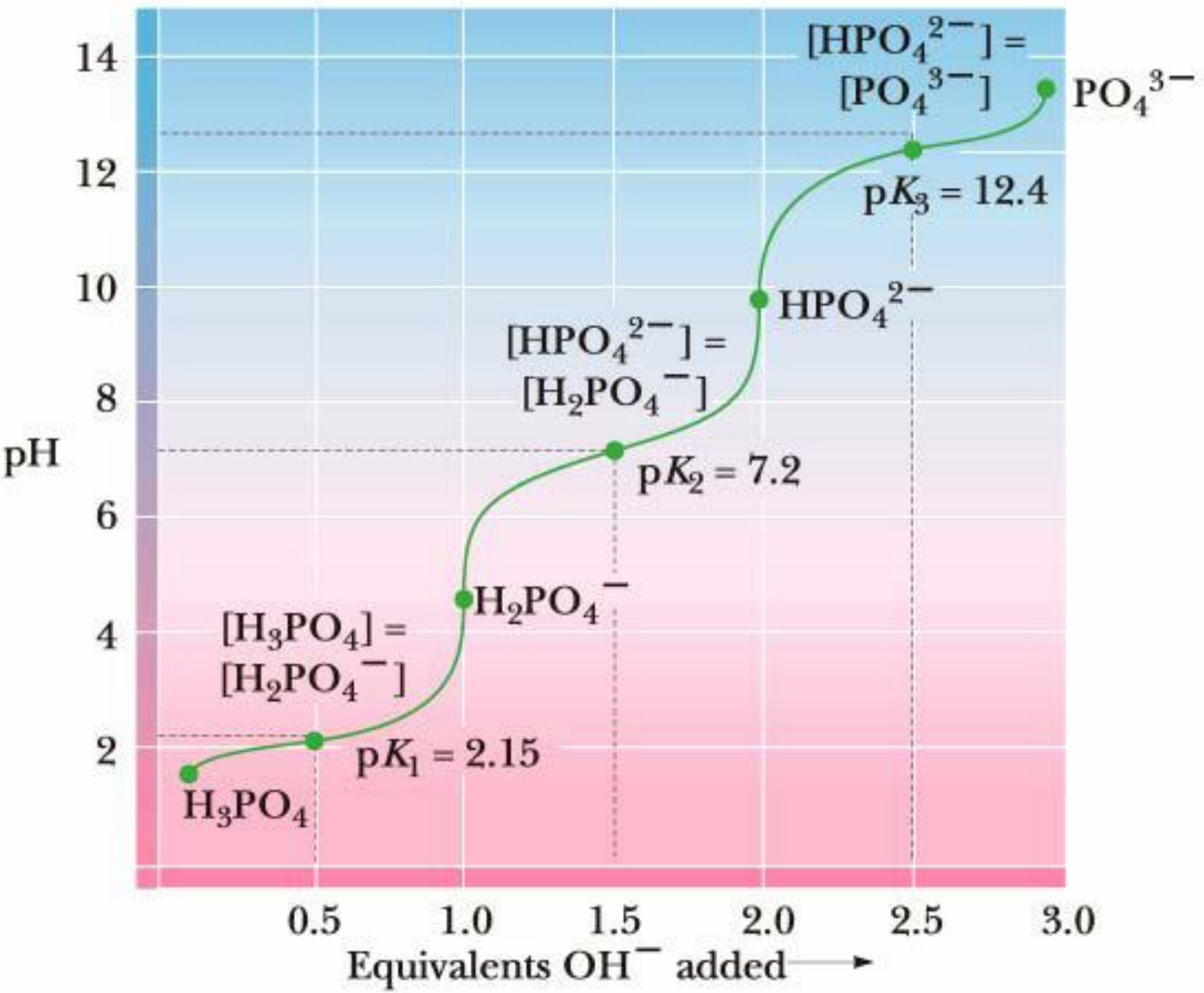
$K_{a2} = 6,2 \times 10^{-8}$

$pK_{a1} = 7,2$

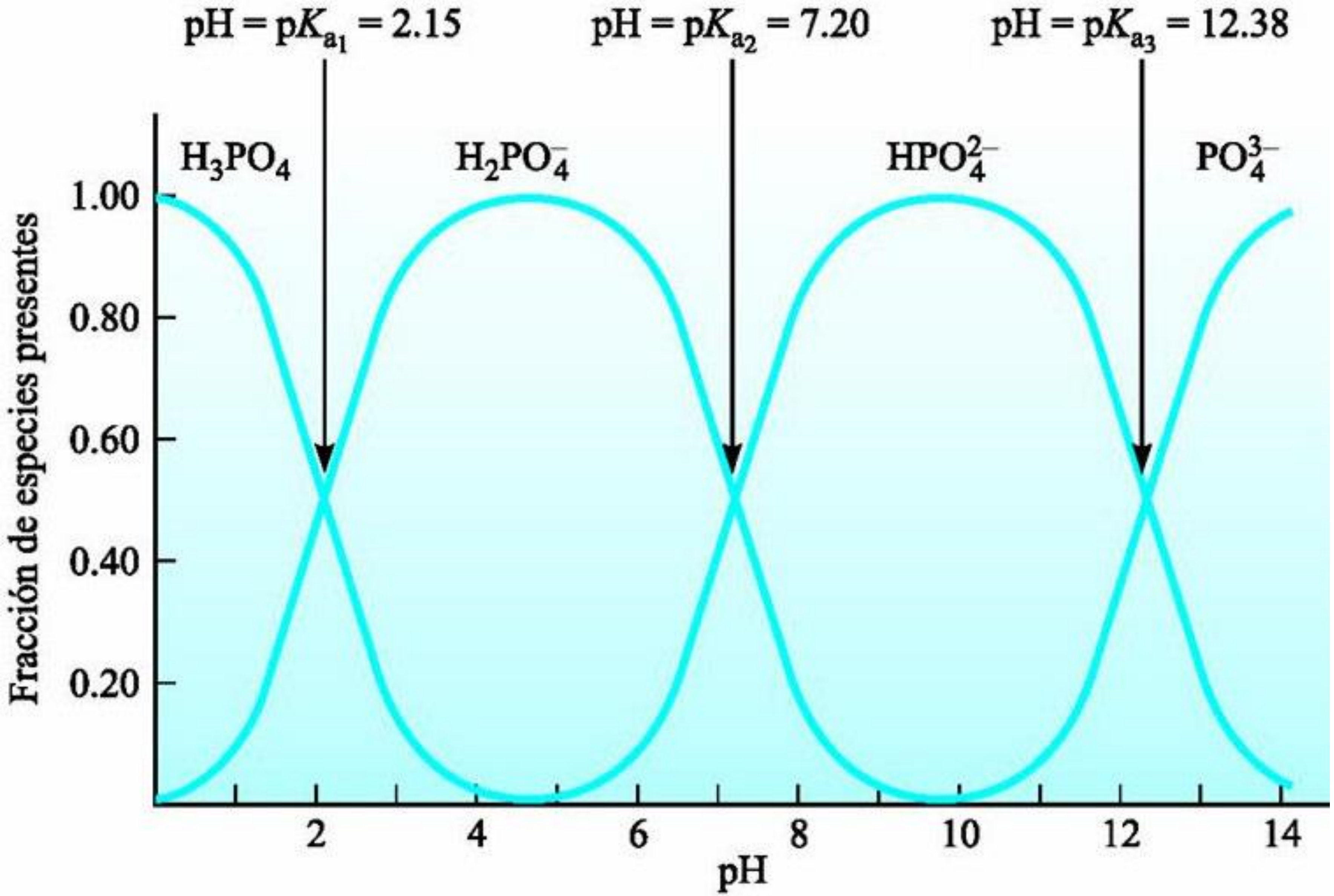
$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$$

$K_{a3} = 4,2 \times 10^{-13}$

$pK_{a2} = 12,4$



14
12
10
8
6
4
2
pH
0.5
1.0
1.5
2.0
2.5
3.0
Equivalents OH^- added
H_3PO_4
$pK_1 = 2.15$
$[H_3PO_4] =$
$[H_2PO_4^-]$
$H_2PO_4^-$
$pK_2 = 7.2$
$[HPO_4^{2-}] =$
$[H_2PO_4^-]$
HPO_4^{2-}
$pK_3 = 12.4$
$[HPO_4^{2-}] =$
$[PO_4^{3-}]$
PO_4^{3-}



$pH = pK_{a_1} = 2.15$
$pH = pK_{a_2} = 7.20$
$pH = pK_{a_3} = 12.38$
H_3PO_4
$H_2PO_4^-$
HPO_4^{2-}
PO_4^{3-}
Fracción de especies presentes
1.00
0.80
0.60
0.40
0.20
2
4
6
8
10
12
14
pH