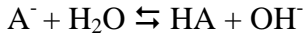
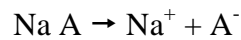


## Sali di acidi deboli

- acido debole + base forte



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$$

1. bilancio di carica

$$[\text{Na}^+] = C = [\text{HA}] + [\text{A}^-]$$

2. bilancio di massa

sostituzione:



3. bilancio protonico

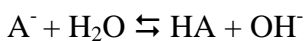
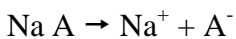
per la base coniugata:

livello di riferimento	$\text{H}_3\text{O}^+$		$\text{HA}$	
		+ $\text{H}^+$		+ $\text{H}^+$
	$\text{H}_2\text{O}$		$\text{A}^-$	
		- $\text{H}^+$		
	$\text{OH}^-$			

$$[\text{H}^+] + [\text{HA}] = [\text{OH}^-]$$

➤ Esempio:

- $\text{NaA}$ ;  $C = 10^{-2} \text{ M}$ ,  $K_a = 10^{-9}$



$$1. \quad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$2. \quad K_w = [\text{H}^+][\text{OH}^-]$$

$$3. \quad [\text{Na}^+] + [\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad \text{bilancio di carica}$$

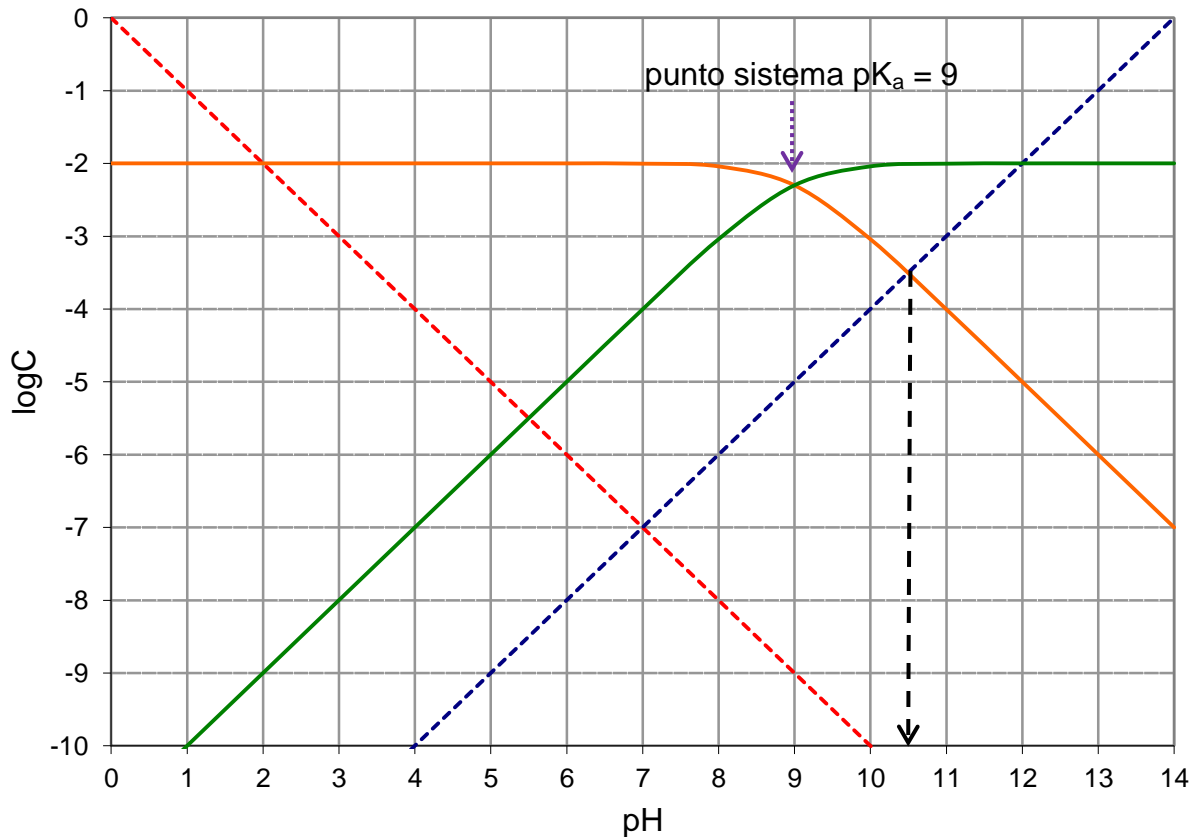
$$4. \quad C_0 = [\text{Na}^+] = [\text{A}^-] + [\text{HA}] \quad \text{bilancio di massa}$$

$$5. \quad [\text{OH}^-] = [\text{HA}] + [\text{H}^+] \quad \text{bilancio protonico}$$

$$K_w = K_a \cdot K_b = 10^{-14}$$

passando ai cologaritmi:  $pK_a + pK_b = 14$

$$pK_b = 14 - 9 = 5$$



I approssimazione: bilancio protonico  $[OH^-] = [H^+] + [HA]$

$[HA] \gg [H^+] \rightarrow [OH^-] = [HA]$

II approssimazione: bilancio di massa  $C_0 = [Na^+] = [HA] + [A^-]$

$[A^-] > [HA] \rightarrow C_0 \cong [A^-]$

sostituzione in  $(K_b = \frac{[HA][OH^-]}{[A^-]})$

dalla I approssimazione:  $K_b = \frac{[OH^-][OH^-]}{[A^-]} = \frac{[OH^-]^2}{[A^-]}$

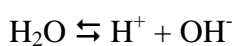
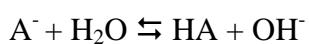
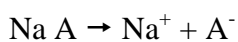
e con la II approssimazione:  $K_b = \frac{[OH^-]^2}{C_0}$ ; quindi

$$[OH^-]^2 = K_b \cdot C_0; [OH^-] = \sqrt{K_b \cdot C_0} = \sqrt{10^{-5} \cdot 10^{-2}} = \sqrt{10^{-7}} = 1 \cdot 10^{-3.5};$$

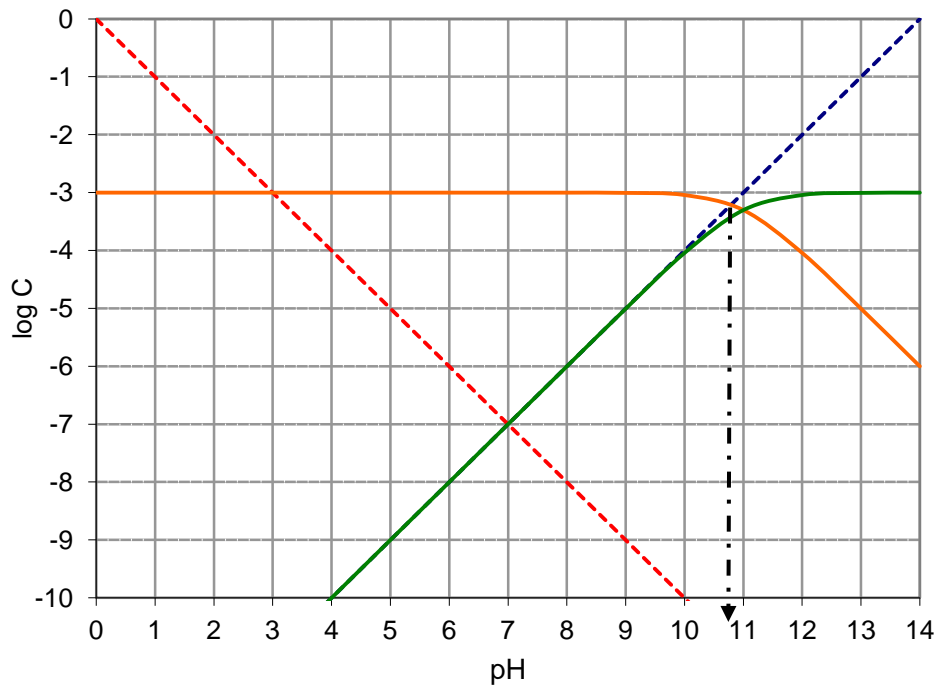
$$pOH = -\log 1 \cdot 10^{-3.5} = 3.5$$

$$pH = 14 - 3.5 = 10.5$$

- **NaA;  $C = 10^{-3}M$ ,  $K_a = 10^{-11}$**



$$pK_b = 3; pK_a = 11$$



I approssimazione: bilancio protonico  $[OH^-] = [H^+] + [HA]$

$[HA] \gg [H^+] \rightarrow [OH^-] = [HA]$

II approssimazione: bilancio di massa  $C_0 = [Na^+] = [HA] + [A^-]$

non valida

dal bilancio di massa  $\rightarrow [A^-] = C_0 - [HA]$

$[A^-] = C_0 - [OH^-]$

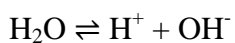
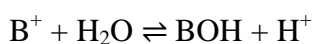
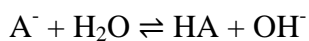
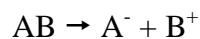
sostituzione in  $K_b \rightarrow K_b = \frac{[OH^-]^2}{C_0 - [OH^-]}$ ;  $[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b C}}{2}$

$$[OH^-] = \frac{-10^{-3} + \sqrt{10^{-6} + 4 \cdot 10^{-3} \cdot 10^{-3}}}{2} = 6.18 \cdot 10^{-4}$$

$$pOH = 4 - \log 6.18 = 3.21116$$

$$pH = 14 - 3.2 = 10.8$$

### 1. acido debole + base debole



in soluzione sono presenti 6 specie,  $A^-$ ,  $HA$ ,  $B^+$ ,  $BOH$ ,  $H^+$ ,  $OH^-$ , per risolvere il problema servono 6 equazioni

$$1. A^- + H_2O \rightleftharpoons HA + OH^- ; \quad K_{idrolisi} = \frac{K_w}{K_{HA}} = \frac{[HA][OH^-]}{[A^-]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

$$2. B^+ + H_2O \rightleftharpoons BOH + H^+ ; \quad K_{idrolisi} = \frac{K_w}{K_{HB}} = \frac{[BOH][H^+]}{[B^+]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$3. H_2O \rightleftharpoons H^+ + OH^- ; K_w = [H^+][OH^-] \quad \text{autoprotolisi}$$

$$4. [B^+] + [H^+] = [A^-] + [OH^-]; \quad \text{bilancio di carica}$$

$$5. C_0 = [A^-] + [HA] = [B^+] + [BOH] \quad \text{bilancio di massa}$$

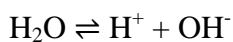
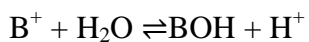
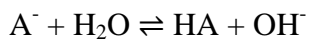
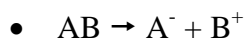
$$6. \quad \text{bilancio protonico,}$$

dal bilancio di materia si ricava  $[B^+] = [A^-] + [HA] - [BOH]$  che si sostituisce nel bilancio di

$$\text{carica } [A^-] \cancel{+} [HA] - [BOH] + [H^+] = [A^-] \cancel{+} [OH^-]$$

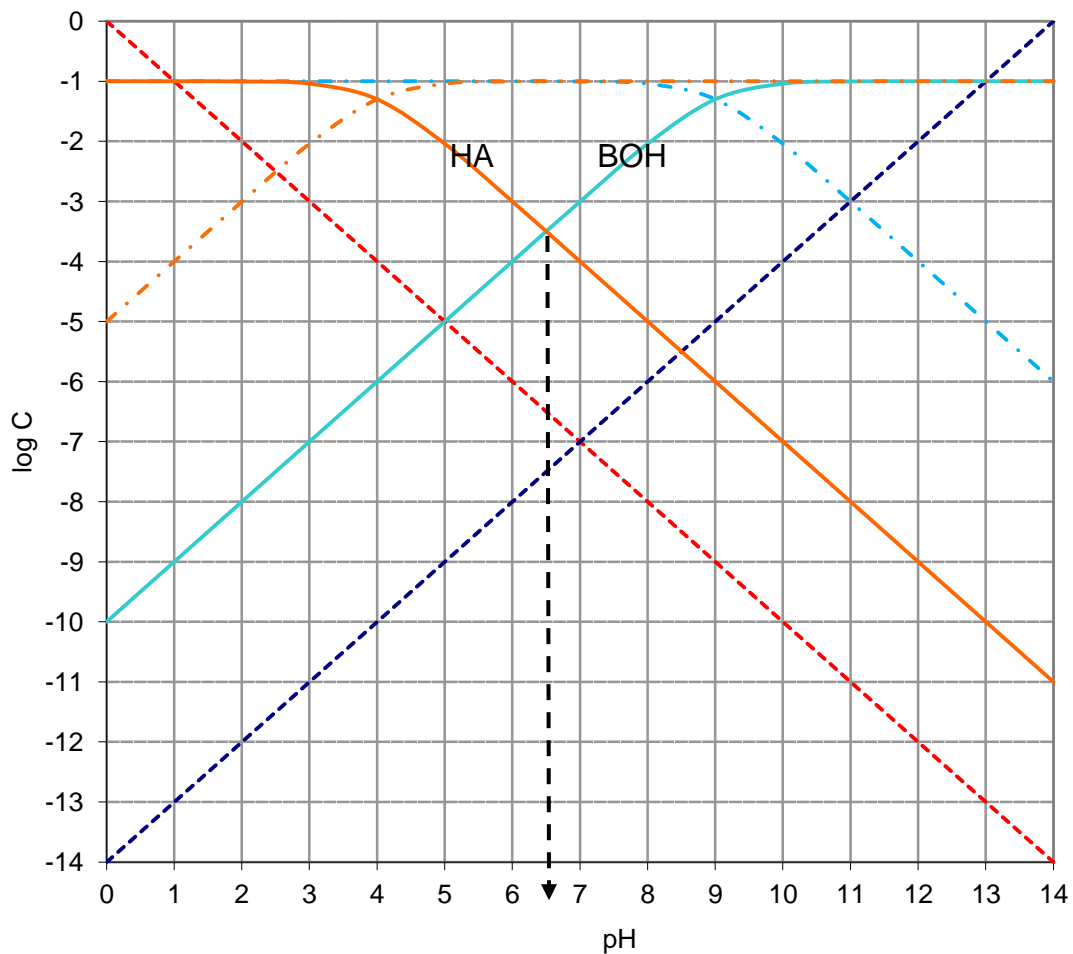
$$[HA] + [H^+] = [BOH] + [OH^-]; \quad \text{bilancio protonico}$$

### ➤ Esempi



$$HA; K_{HA} = 10^{-4}; \text{ e } BOH; K_{BOH} = 10^{-5}; C_0 = 0.1 \text{ M}$$

- grafici logaritmici: sovrapposizione dei singoli diagrammi di distribuzione (HA e BOH)



I approssimazione: **bilancio protonico**  $[H^+] + [HA] = [OH^-] + [BOH]$

$[HA] \gg [H^+]$  e  $[BOH] \gg [OH^-]$ ;  $\rightarrow [HA] = [BOH]$

II approssimazione: bilancio di massa  $C_0 = [BOH] + [B^+] = [HA] + [A^-]$

$[A^-] \gg [HA]$  e  $[B^+] \gg [BOH]$ ;  $\rightarrow [A^-] = C_0$  e  $[B^+] = C_0$ ;  $\rightarrow [A^-] = [B^+]$

dalla legge dell'equilibrio di massa 1:  $[HA] = \frac{K_w}{K_{HA}} \cdot \frac{[A^-]}{[OH^-]} = \frac{K_w}{K_{HA}} \cdot \frac{[A^-][H^+]}{K_w} = \frac{C_0[H^+]}{K_{HA}}$

dalle legge dell'equilibrio di massa 2:  $[BOH] = \frac{K_w}{K_{BOH}} \cdot \frac{[B^-]}{[H^+]} = \frac{K_w \cdot C_0}{K_{BOH}[H^+]}$

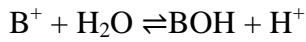
dal bilancio protonico:  $[HA] = [BOH]$  per sostituzione:

$$\frac{C_0[H^+]}{K_{HA}} = \frac{K_w C_0}{K_{BOH}[H^+]}; [H^+] = \sqrt{\frac{K_w}{K_{BOH}} \cdot K_{HA}}$$

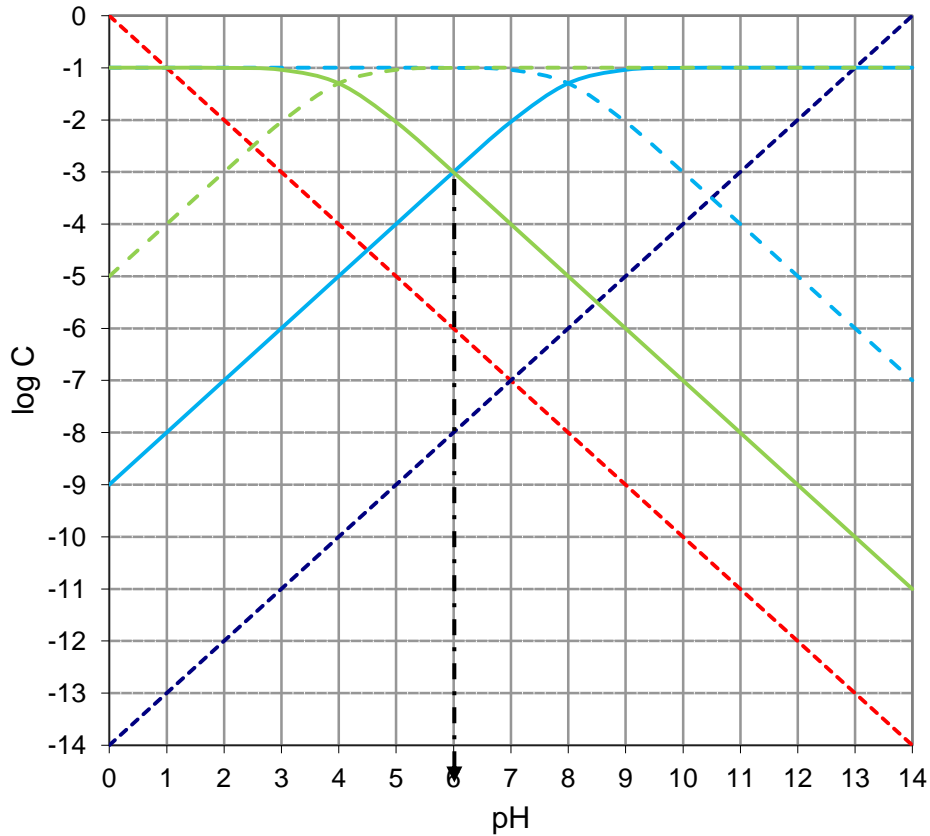
$$[H^+] = \sqrt{10^{-9} \cdot 10^{-4}} = \sqrt{10^{-13}} = 10^{-6.5}$$

$$\text{pH} = 6.5$$

- $AB \rightarrow A^- + B^+$   
 $A^- + H_2O \rightleftharpoons HA + OH^-$



HA;  $K_{HA} = 10^{-4}$ ; e BOH;  $K_{BOH} = 10^{-6}$ ;  $C_0 = 0.1 \text{ M}$



I approssimazione: **bilancio protonico**  $[H^+] + [HA] = [OH^-] + [BOH]$

$[HA] \gg [H^+]$  e  $[BOH] \gg [OH^-]$ ;  $\rightarrow [HA] = [BOH]$

II approssimazione: bilancio di massa  $C_0 = [BOH] + [B^+] = [HA] + [A^-]$

$[A^-] \gg [HA]$  e  $[B^+] \gg [BOH]$ ;  $\rightarrow [A^-] = C_0$  e  $[B^+] = C_0$ ;  $\rightarrow [A^-] = [B^+]$

dalla legge dell'equilibrio di massa 1:  $[HA] = \frac{K_w}{K_{HA}} \cdot \frac{[A^-]}{[OH^-]} = \frac{K_w}{K_{HA}} \cdot \frac{[A^-][H^+]}{K_w} = \frac{C_0[H^+]}{K_{HA}}$

dalle legge dell'equilibrio di massa 2:  $[BOH] = \frac{K_w}{K_{BOH}} \cdot \frac{[B^+]}{[H^+]} = \frac{K_w \cdot C_0}{K_{BOH}[H^+]}$

dal bilancio protonico:  $[HA] = [BOH]$ , per sostituzione:

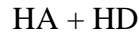
$$\frac{C_0[H^+]}{K_{HA}} = \frac{K_w C_0}{K_{BOH}[H^+]}; [H^+] = \sqrt{\frac{K_w}{K_{BOH}} \cdot K_{HA}}$$

$$[H^+] = \sqrt{10^{-8} \cdot 10^{-4}} = \sqrt{10^{-12}} = 10^{-6}$$

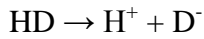
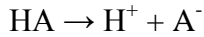
$$\text{pH} = 6$$

### Miscela di 2 acidi forti

Si consideri una miscela formata da un acido forte HA ed un altro acido forte HD,



in soluzione acquosa si verifica la completa dissociazione degli acidi:



in soluzione sono presenti 4 specie,  $\text{A}^-$ ,  $\text{D}^-$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , per risolvere il problema servono 4 equazioni:

1.  $[\text{H}^+][\text{OH}^-] = K_w$  *autoprotolisi*
2.  $[\text{H}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{D}^-]$  *bilancio protonico*
3.  $[\text{A}^-] = [\text{HA}]_0 = C_{0A}$  *bilancio di massa per A*
4.  $[\text{D}^-] = [\text{HD}]_0 = C_{0D}$  *bilancio di massa per D*

dalla 2.) si ricava che  $[\text{D}^-] = [\text{H}^+] - [\text{A}^-] - [\text{OH}^-]$ , quindi

$$C_{0D} - [\text{H}^+] + C_{0A} + K_w/[\text{H}^+] = 0$$

$$([\text{H}^+])^2 - (C_{0A} + C_{0D})[\text{H}^+] - K_w = 0$$

$$[\text{H}^+] = \frac{+C + \sqrt{C^2 + 4K_w}}{2} \text{ dove } C = (C_{0A} + C_{0D})$$

equazione uguale a quella generale per l'acido forte.

si possono fare le approssimazioni !!!!!

#### ➤ Esempio

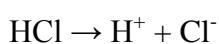
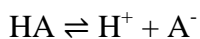
##### ○ HA + HD

$$\text{HA } C_0 = 10^{-2}\text{M}; \text{ HD } C_0 = 10^{-2}\text{M}$$

$$\text{pH} = -\log(C_{0A} + C_{0D}) = -\log(10^{-2} + 10^{-2}) = -\log 2 \cdot 10^{-2} = 2 - \log 2 = 2 - 0.3 = 1.7$$

### Miscela di acido forte e acido debole

Si consideri una miscela formata da un acido forte HCl ed un acido debole HA, in soluzione acquosa sono presenti i seguenti equilibri:



in soluzione sono presenti 5 specie, HA,  $\text{A}^-$ ,  $\text{Cl}^-$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , per risolvere il problema servono 5 equazioni:

1.  $K_a = \frac{[H^+][A^-]}{[HA]}$
2.  $K_w = [H^+][OH^-]$
3.  $[H^+] = [A^-] + [Cl^-] + [OH^-]$       *bilancio di carica = bilancio protonico*
4.  $C_0 = [A^-] + [HA]$       *bilancio di massa per A*
5.  $C_0 = [Cl^-]$       *bilancio di massa per Cl*

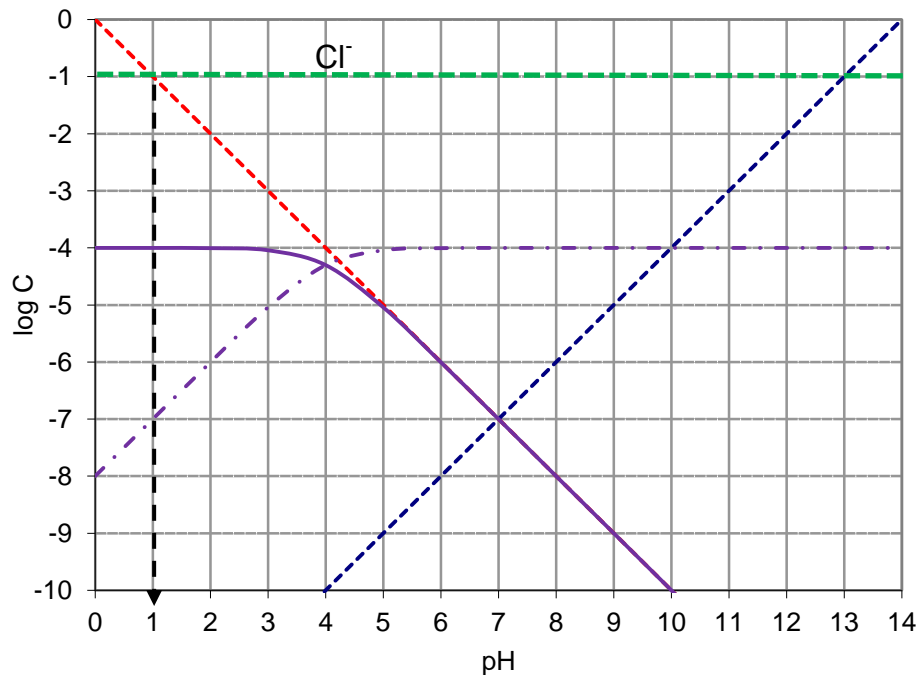
si possono verificare più frequentemente le seguenti situazioni:

➤ Esempi

1.  $C_0 [HCl] \gg C_0 [HA]$

$[H^+]$  della soluzione è uguale alla  $[H^+]$  dell'acido forte  $\rightarrow [H^+]_{tot} = [H^+]_{HCl}$

- $C_0 [HCl] = 10^{-1}$ ;  $C_0 [HA] = 10^{-4}$ ,  $K_a = 10^{-4}$



I approssimazione: **bilancio protonico**  $[H^+] = [OH^-] + [A^-] + [Cl^-]$

$[Cl^-] \gg [OH^-]$  e  $[Cl^-] \gg [A^-]$ ;  $\rightarrow [H^+] = [Cl^-]$

II approssimazione: bilancio di massa  $C_{0HCl} = [HCl]_0 = [Cl^-]$

$[H^+] = C_{0HCl}$

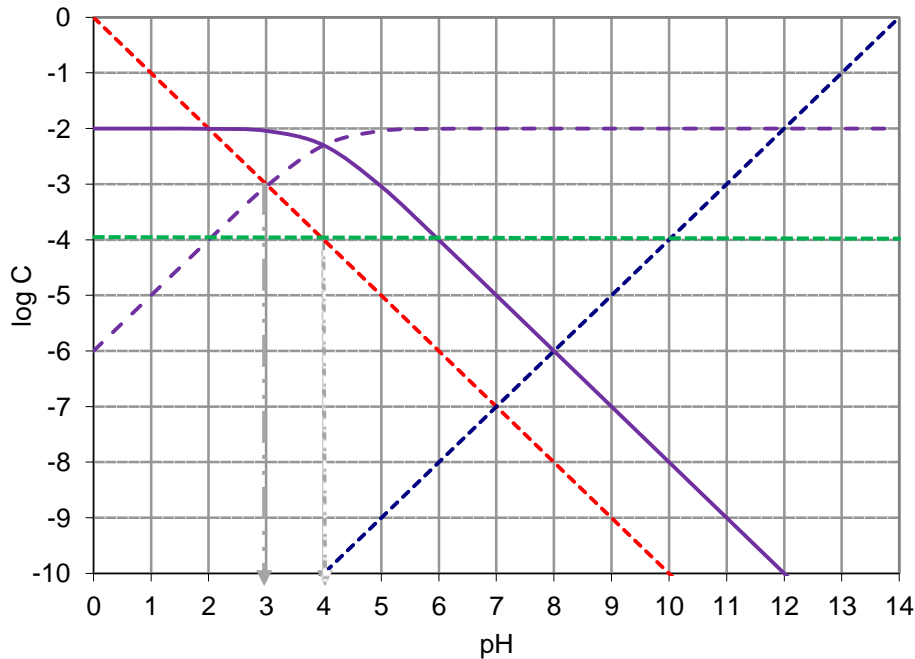
$[H^+] = 10^{-1}$

pH = 1

2.  $C_0 [HCl] \ll C_0 [HA]$ ,  $C_0 [HA] \gg C_0 [HCl]$

- $C_0 [HCl] = 10^{-4}$ ;  $C_0 [HA] = 10^{-2}$ ,  $K_a = 10^{-4}$





dal grafico logaritmico, considerando separatamente ogni specie acida risulta che il pH di HCl = 4 e il pH di HA = 3

I approssimazione: **bilancio protonico**  $[H^+] = [OH^-] + [A^-] + [Cl^-]$

$[A^-] \gg [OH^-]$ ;  $\rightarrow [H^+] = [A^-] + [Cl^-]$  ma  $[Cl^-] = C_{0[HCl]}$ ;  $\rightarrow [H^+] = [A^-] + C_{0[HCl]}$ ;

$[A^-] = [H^+] + C_{0[HCl]}$ ;

II approssimazione: bilancio di massa  $C_0 = [HA]_0 = [HA] + [A^-]$

$[HA] > [A^-] \rightarrow C_0 \cong [HA]$  (10% di errore)

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

$$[H^+]^2 - [H^+]C_{0[HCl]} - K_a C_{0[HA]} = 0$$

$$[H^+] = \frac{C_{0[HCl]} + \sqrt{(C_{0[HCl]})^2 + 4K_a C_{0[HA]}}}{2} = \frac{10^{-4} + \sqrt{(10^{-4})^2 + 4 \cdot 10^{-4} \cdot 10^{-2}}}{2}$$

$$= 1.05125 \cdot 10^{-3}$$

$$pH = 3 - \log 1.05125 = 3 - 0.02171 = 2.97829 = 2.98$$

non utilizzando il sistema d'equazioni sopra riportate, ma:

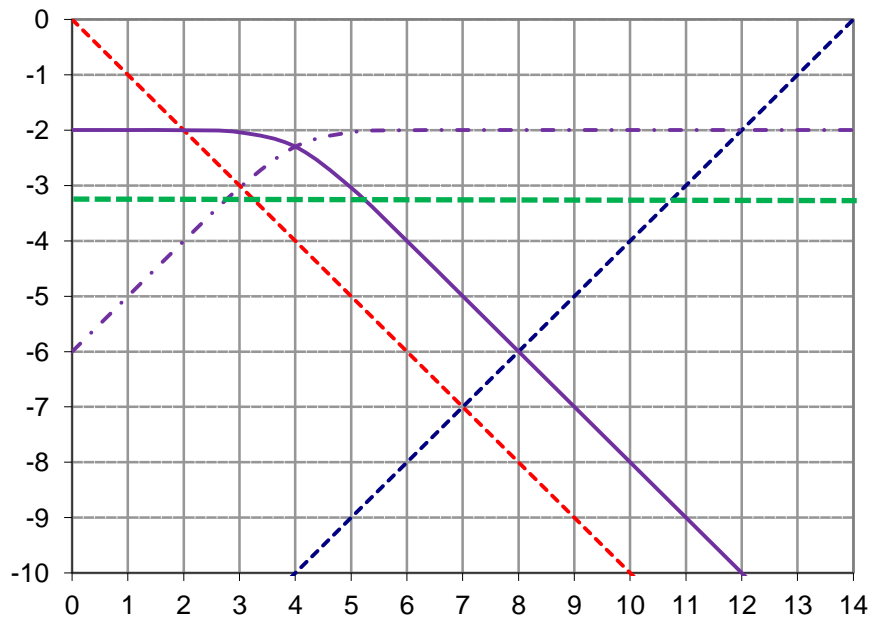
$$pH = -\log (C_{0[HCl]} + [H^+] \text{ di HA})$$

$$pH = -\log (10^{-4} + 10^{-3}) = -\log (1.1 \cdot 10^{-3}) = 3 - \log 1.1 = 3 - 0.04139 = 2.9586 = 2.96$$

- $C_0 [HCl] = 5 \cdot 10^{-4}$ ;  $C_0 [HA] = 10^{-2}$ ,  $K_a = 10^{-4}$

$C_0 [HCl] \ll C_0 [HA]$

$$\log C_0 [\text{HCl}] = -3.3$$



dal grafico logaritmico, considerando separatamente ogni specie acida risulta che il pH di HCl = 3.3 e il pH di HA = 3

I approssimazione: **bilancio protonico**  $[\text{H}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{Cl}^-]$

$[\text{A}^-] \gg [\text{OH}^-]$ ;  $\rightarrow [\text{H}^+] = [\text{A}^-] + [\text{Cl}^-]$  ma  $[\text{Cl}^-] = C_0 [\text{HCl}]$ ;  $\rightarrow [\text{H}^+] = [\text{A}^-] + C_0 [\text{HCl}]$ ;

$[\text{A}^-] = [\text{H}^+] - C_0 [\text{HCl}]$ ;

II approssimazione: bilancio di massa  $C_0 = [\text{HA}]_0 = [\text{HA}] + [\text{A}^-]$

$[\text{HA}] > [\text{A}^-] \rightarrow C_0 \cong [\text{HA}]$  (10% di errore)

sostituzione in  $K_a = \frac{[\text{H}^+][\text{H}^+] - C_0 [\text{HCl}]}{C_0 [\text{HA}]}$

$$[\text{H}^+]^2 - [\text{H}^+]C_0 [\text{HCl}] - K_a C_0 [\text{HA}] = 0$$

$$[\text{H}^+] = \frac{C_0 [\text{HCl}] + \sqrt{(C_0 [\text{HCl}])^2 + 4K_a C_0 [\text{HA}]}}{2} = \frac{5 \cdot 10^{-4} + \sqrt{(5 \cdot 10^{-4})^2 + 4 \cdot 10^{-4} \cdot 10^{-2}}}{2}$$

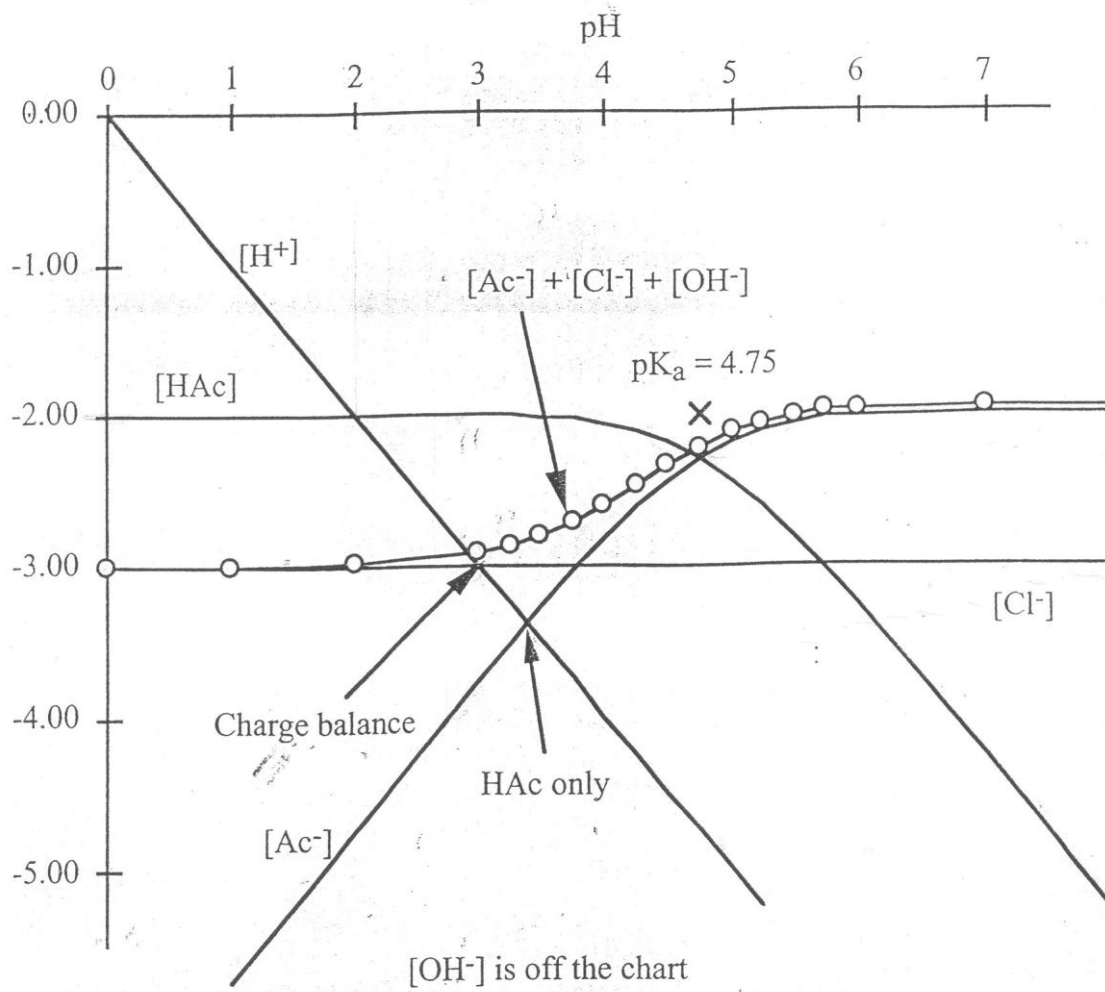
$$= 1.28 \cdot 10^{-3}$$

$$\text{pH} = 3 - \log 1.28 = 3 - 0.1072 = 2.8928 = 2.89$$

non utilizzando il sistema d'equazioni sopra riportate, ma:

$$\text{pH} = -\log (C_0 [\text{HCl}] + [\text{H}^+] \text{ di HA})$$

$$\text{pH} = -\log (5 \cdot 10^{-4} + 10^{-3}) = -\log (1.5 \cdot 10^{-3}) = 3 - \log 1.5 = 3 - 0.176 = 2.824 = 2.82$$

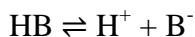
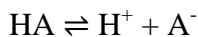


## Miscela di due acidi deboli monoprotici

Si consideri una miscela formata da due acidi deboli HA HB,



in soluzione acquosa si verifica la parziale dissociazione degli acidi:



in soluzione sono presenti 6 specie, HA, HB, A<sup>-</sup>, B<sup>-</sup>, H<sup>+</sup>, OH<sup>-</sup>, per risolvere il problema servono 6 equazioni:

$$1. K_{HA} = \frac{[H^+][A^-]}{[HA]}$$

$$2. K_{HB} = \frac{[H^+][B^-]}{[HB]}$$

$$3. [H^+][OH^-] = K_w \quad \text{autoprotolisi}$$

$$4. [H^+] = [OH^-] + [A^-] + [B^-] \quad \text{bilancio di carica = bilancio protonico}$$

livello di riferimento	H <sub>3</sub> O <sup>+</sup>			
	↪	+ H <sup>+</sup>		
	H <sub>2</sub> O		HA; HB	
	↩	- H <sup>+</sup>		
	OH <sup>-</sup>		A <sup>-</sup> ; B <sup>-</sup>	↩ - H <sup>+</sup>

$$[H^+] = [OH^-] + [A^-] + [B^-]$$

$$5. C_{0HA} = [HA]_0 = [A^-] + [HA] \quad \text{bilancio di massa per A}$$

$$6. C_{0HB} = [HB]_0 = [B^-] + [HB] \quad \text{bilancio di massa per B}$$

come si risolve?

si ricava [A<sup>-</sup>] e [B<sup>-</sup>] in funzione delle rispettive K<sub>eq</sub> e delle C<sub>0</sub>

quindi

$$\text{dalla 5.} \rightarrow [HA] = C_{0A} - [A^-] \text{ e sostituisco nella 1.} \rightarrow K_{HA} = \frac{[H^+][A^-]}{C_{0A} - [A^-]}$$

$$K_{HA}C_{0A} - K_{HA}[A^-] - [H^+][A^-] = 0; \rightarrow [A^-] = \frac{K_{HA}C_{0A}}{K_{HA} + [H^+]}$$

$$\text{dalla 6.} \rightarrow [HB] = C_{0B} - [B^-] \text{ e sostituisco nella 2.} \rightarrow K_{HB} = \frac{[H^+][B^-]}{C_{0B} - [B^-]}$$

$$K_{HB}C_{0B} - K_{HB}[B^-] - [H^+][B^-] = 0; \rightarrow [B^-] = \frac{K_{HB}C_{0B}}{K_{HB} + [H^+]}$$

$$\text{dalla 3.} \rightarrow [OH^-] = \frac{K_w}{[H^+]}$$

$$\text{sostituzione nella 4., (bilancio protonico)} \rightarrow [H^+] = \frac{K_w}{[H^+]} + \frac{K_{HA}C_{0A}}{K_{HA} + [H^+]} + \frac{K_{HB}C_{0B}}{K_{HB} + [H^+]}$$

risolvendo si ottiene una equazione di quarto grado!!

si possono fare le approssimazioni !!!!!

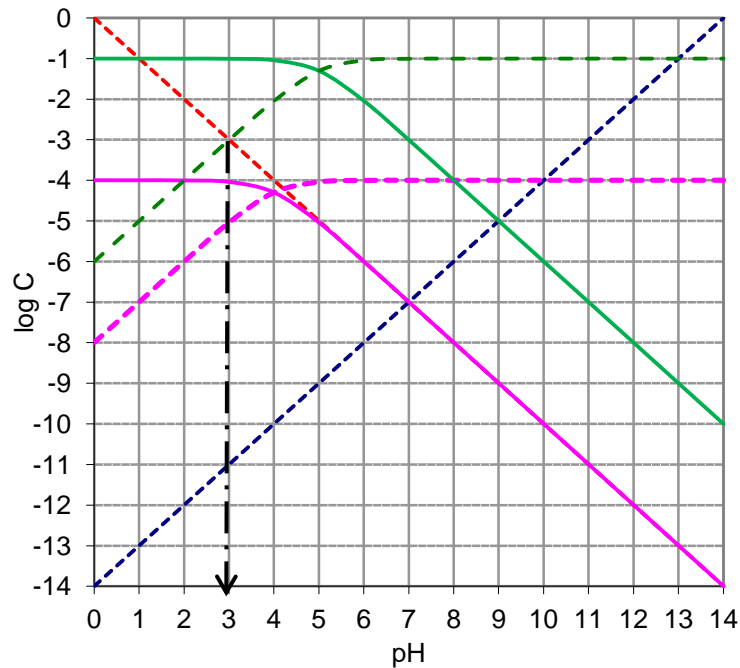
○ grafici logaritmici: sovrapposizione dei singoli diagrammi di distribuzione (HA e HB)

➤ Esempi

- $C_0 [\text{HA}] = 10^{-1}$ ;  $C_0 [\text{HB}] = 10^{-4}$ ;  $K_{\text{HA}} = 10^{-5}$ ;  $K_{\text{HB}} = 10^{-4}$

$C_0 [\text{HA}] \gg C_0 [\text{HB}]$  e  $K_{\text{HA}} \cong K_{\text{HB}}$

**dipendenza da  $C_{0\text{HA}}$**



I approssimazione: **bilancio protonico**  $[\text{H}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-]$

$[\text{A}^-] \gg [\text{OH}^-]$  e  $[\text{A}^-] > [\text{B}^-] \rightarrow [\text{H}^+] = [\text{A}^-]$

II approssimazione: bilancio di massa  $C_{0\text{HA}} = [\text{HA}]_0 = [\text{HA}] + [\text{A}^-]$

$[\text{HA}] \gg [\text{A}^-] \rightarrow C_{0\text{HA}} \cong [\text{HA}]$

sostituzione in  $K_{\text{HA}}$

$$[\text{H}^+] = \sqrt{K_{\text{HA}} \cdot C_{0\text{HA}}} = \sqrt{10^{-5} \cdot 10^{-1}} = \sqrt{10^{-6}} = 1 \cdot 10^{-3}; \text{pH} = 3$$

- $C_0 [\text{HA}] = 10^{-2}$ ;  $C_0 [\text{HB}] = 10^{-1}$ ;  $K_{\text{HA}} = 10^{-4}$ ;  $K_{\text{HB}} = 10^{-9}$

$K_{\text{HA}} \gg K_{\text{HB}}$  e  $C_0 [\text{HA}] \cong C_0 [\text{HB}]$

**dipendenza da  $K_{\text{HA}}$**

I approssimazione: **bilancio protonico**  $[\text{H}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-]$

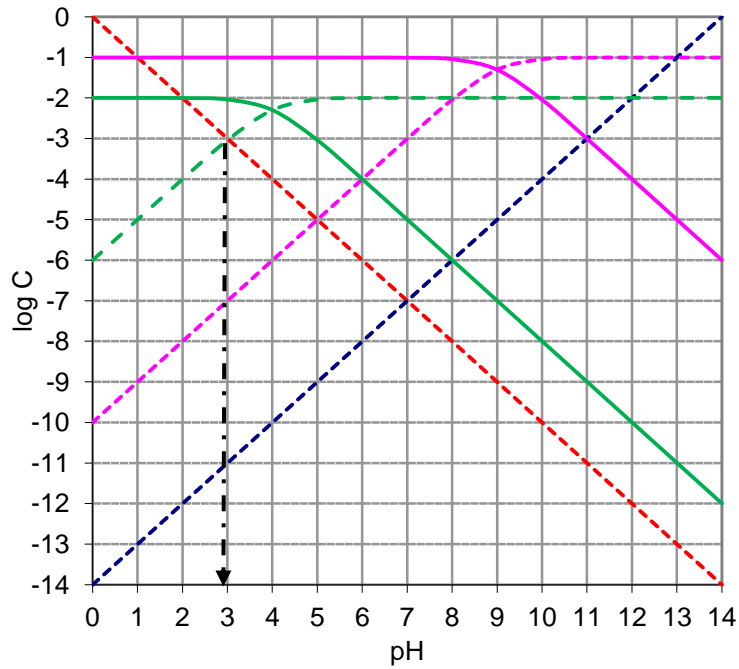
$[\text{A}^-] \gg [\text{OH}^-]$  e  $[\text{A}^-] \gg [\text{B}^-] \rightarrow [\text{H}^+] = [\text{A}^-]$

II approssimazione: bilancio di massa  $C_{0\text{HA}} = [\text{HA}]_0 = [\text{HA}] + [\text{A}^-]$

$[\text{HA}] > [\text{A}^-] \rightarrow C_{0\text{HA}} \cong [\text{HA}]$  (10% di errore)

sostituzione in  $K_{\text{HA}}$

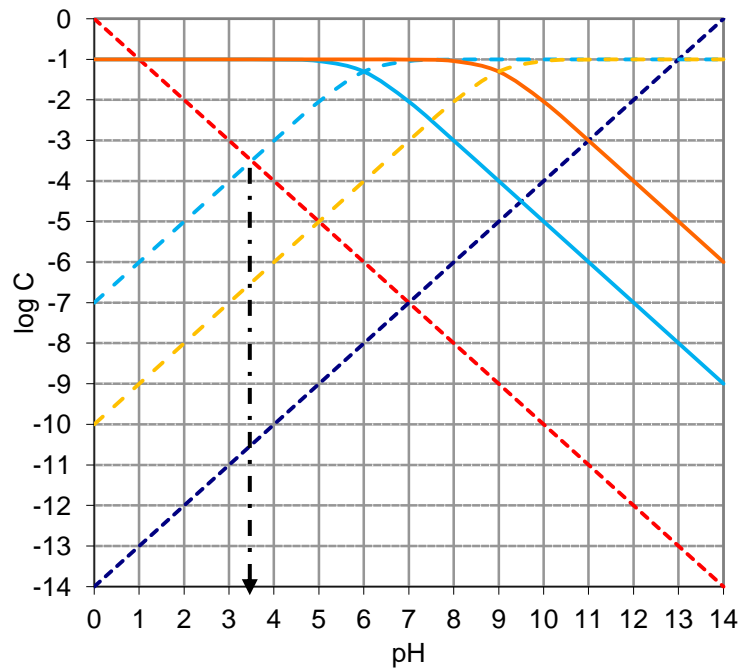
$$[\text{H}^+] = \sqrt{K_{\text{HA}} \cdot C_{0\text{HA}}} = \sqrt{10^{-4} \cdot 10^{-2}} = \sqrt{10^{-6}} = 1 \cdot 10^{-3}; \text{pH} = 3$$



- $C_0 [\text{HA}] = C_0 [\text{HB}] = 10^{-1}$ ;  $K_{\text{HA}} = 10^{-9}$ ;  $K_{\text{HB}} = 10^{-6}$

$K_{\text{HA}} \ll K_{\text{HB}}$  e  $C_0 [\text{HA}] \cong C_0 [\text{HB}]$

**dipendenza da  $K_{\text{HB}}$**



I approssimazione: **bilancio protonico**  $[\text{H}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-]$

$[\text{B}^-] \gg [\text{OH}^-]$  e  $[\text{B}^-] \gg [\text{A}^-] \rightarrow [\text{H}^+] = [\text{B}^-]$

II approssimazione: bilancio di massa  $C_{0\text{HB}} = [\text{HB}]_0 = [\text{HB}] + [\text{B}^-]$

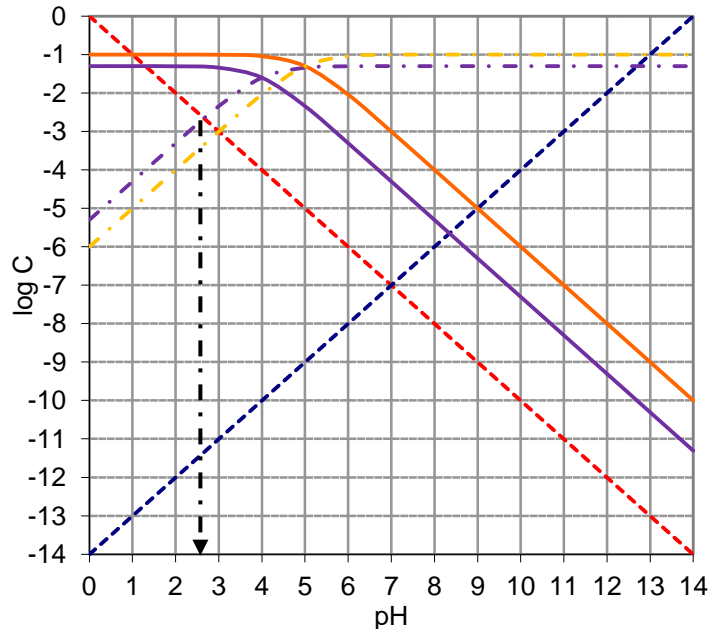
$[\text{HB}] \gg [\text{B}^-] \rightarrow C_{0\text{HB}} = [\text{HB}]$

sostituzione in  $K_{\text{HB}}$

$$[H^+] = \sqrt{K_{HB} \cdot C_{OHB}} = \sqrt{10^{-6} \cdot 10^{-1}} = \sqrt{10^{-7}} = 1 \cdot 10^{-3,5}; \text{pH} = 3.5$$

- $C_0 [\text{HA}] = 10^{-1}$ ;  $C_0 [\text{HB}] = 5 \cdot 10^{-2}$ ;  $K_{\text{HA}} = 10^{-5}$ ;  $K_{\text{HB}} = 10^{-4}$

$$\underline{K_{\text{HA}} \cong K_{\text{HB}} \text{ e } C_0 [\text{HA}] \cong C_0 [\text{HB}]}$$



I approssimazione: **bilancio protonico**  $[H^+] = [\text{OH}^-] + [A^-] + [B^-]$

$$[A^-] \gg [\text{OH}^-] \text{ e } [B^-] \gg [\text{OH}^-] \rightarrow [H^+] = [A^-] + [B^-]$$

II approssimazione: bilancio di massa  $C_{\text{OHB}} = [\text{HB}]_0 = [\text{HB}] + [B^-]$ ,  $C_{\text{OHA}} = [\text{HA}]_0 = [\text{HA}] + [A^-]$

$$[\text{HA}] \gg [A^-] \rightarrow C_{\text{OHA}} = [\text{HA}] \text{ e } [\text{HB}] \gg [B^-] \rightarrow C_{\text{OHB}} = [\text{HB}]$$

$$\text{dalla } K_{\text{HA}} \rightarrow [A^-] = \frac{K_{\text{HA}} C_{\text{OHA}}}{[H^+]} \text{ e dalla } K_{\text{HB}} \rightarrow [B^-] = \frac{K_{\text{HB}} C_{\text{OHB}}}{[H^+]}$$

sostituzione nel bilancio protonico :

$$[H^+] = \frac{K_{\text{HA}} C_{\text{OHA}}}{[H^+]} + \frac{K_{\text{HB}} C_{\text{OHB}}}{[H^+]}; [H^+]^2 = K_{\text{HA}} C_{\text{OHA}} + K_{\text{HB}} C_{\text{OHB}}; [H^+] = \sqrt{K_{\text{HA}} C_{\text{OHA}} + K_{\text{HB}} C_{\text{OHB}}}$$

$$[H^+] = \sqrt{10^{-5} \cdot 10^{-1} + 10^{-4} \cdot 5 \cdot 10^{-2}} = \sqrt{10^{-6}(1 + 5)} = 10^{-3} \sqrt{6} = 2.449 \cdot 10^{-3}$$

$$\text{pH} = 3 - \log 2.449 = 3 - 0.389 = 2.611$$

- $C_0 [\text{HA}] = 10^{-1}$ ;  $C_0 [\text{HB}] = 10^{-2}$ ;  $K_{\text{HA}} = 10^{-5}$ ;  $K_{\text{HB}} = 10^{-4}$

$$\underline{K_{\text{HA}} \cong K_{\text{HB}} \text{ e } C_0 [\text{HA}] \cong C_0 [\text{HB}]}$$

I approssimazione: **bilancio protonico**  $[H^+] = [\text{OH}^-] + [A^-] + [B^-]$

$$[A^-] \gg [\text{OH}^-] \text{ e } [B^-] \gg [\text{OH}^-] \rightarrow [H^+] = [A^-] + [B^-]$$

II approssimazione: bilancio di massa  $C_{\text{OHB}} = [\text{HB}]_0 = [\text{HB}] + [B^-]$ ,  $C_{\text{OHA}} = [\text{HA}]_0 = [\text{HA}] + [A^-]$

$$[\text{HA}] \gg [A^-] \rightarrow C_{\text{OHA}} = [\text{HA}] \text{ e } [\text{HB}] \gg [B^-] \rightarrow C_{\text{OHB}} = [\text{HB}]$$

$$\text{dalla } K_{\text{HA}} \rightarrow [A^-] = \frac{K_{\text{HA}} C_{\text{OHA}}}{[H^+]} \text{ e dalla } K_{\text{HB}} \rightarrow [B^-] = \frac{K_{\text{HB}} C_{\text{OHB}}}{[H^+]}$$

sostituzione nel bilancio protonico :

$$[H^+] = \frac{K_{HA}C_{OHA}}{[H^+]} + \frac{K_{HB}C_{OHB}}{[H^+]};$$

$$[H^+]^2 = K_{HA}C_{OHA} + K_{HB}C_{OHB};$$

$$[H^+] = \sqrt{K_{HA}C_{OHA} + K_{HB}C_{OHB}}$$

$$[H^+] = \sqrt{10^{-5} \cdot 10^{-1} + 10^{-5} \cdot 10^{-2}} = \sqrt{10^{-6} + 10^{-7}} = \sqrt{1.1 \cdot 10^{-6}} = 1.05 \cdot 10^{-3}$$

$$\text{pH} = 2.98$$

