# REAZIONI IN SOLUZIONE

- ACIDO-BASE ⇨ SCAMBIO DI PROTONI

$$HA + B \leftrightarrows A^- + BH^+$$

- REDOX ⇨ SCAMBIO DI ELETTRONI

$$A_{OX} + B_{RED} \leftrightarrows A_{RED} + B_{OX}$$

- EQUILIBRI DI SOLUBILITÀ

$$CatAn_{(s)} \leftrightarrows Cat^+_{(aq)} + An^-_{(aq)}$$

# REAZIONI ACIDO-BASE

## ARRHENIUS

ACIDO ⇨ LIBERA IONI $H^+$

$HCl \rightarrow H^+ + Cl^-$

BASE ⇨ LIBERA IONI $OH^-$

$NaOH \rightarrow Na^+ + OH^-$ BASE

$NH_3 + H_2O \rightarrow NH_4OH$

$NH_4OH \leftrightarrows NH_4^+ + OH^-$

BRÖNSTED E LOWRY

ACIDO ⇨ HA ⇨ SPECIE CAPACE DI DONARE IONI $H^+$

BASE ⇨B ⇨ SPECIE CAPACE DI ACCETTARE IONI $H^+$

BASE ACIDO CONIUGATO

$$HA + B \leftrightarrows A^- + BH^+$$

ACIDO BASE CONIUGATA

$$HNO_2 + H_2O \leftrightarrows NO_2^- + H_3O^+$$

acido1 base2 base1 acido2

$H_3O^+$ = IONE IDROSSONIO (OSSONIO)

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

base1 acido2 acido1 base2

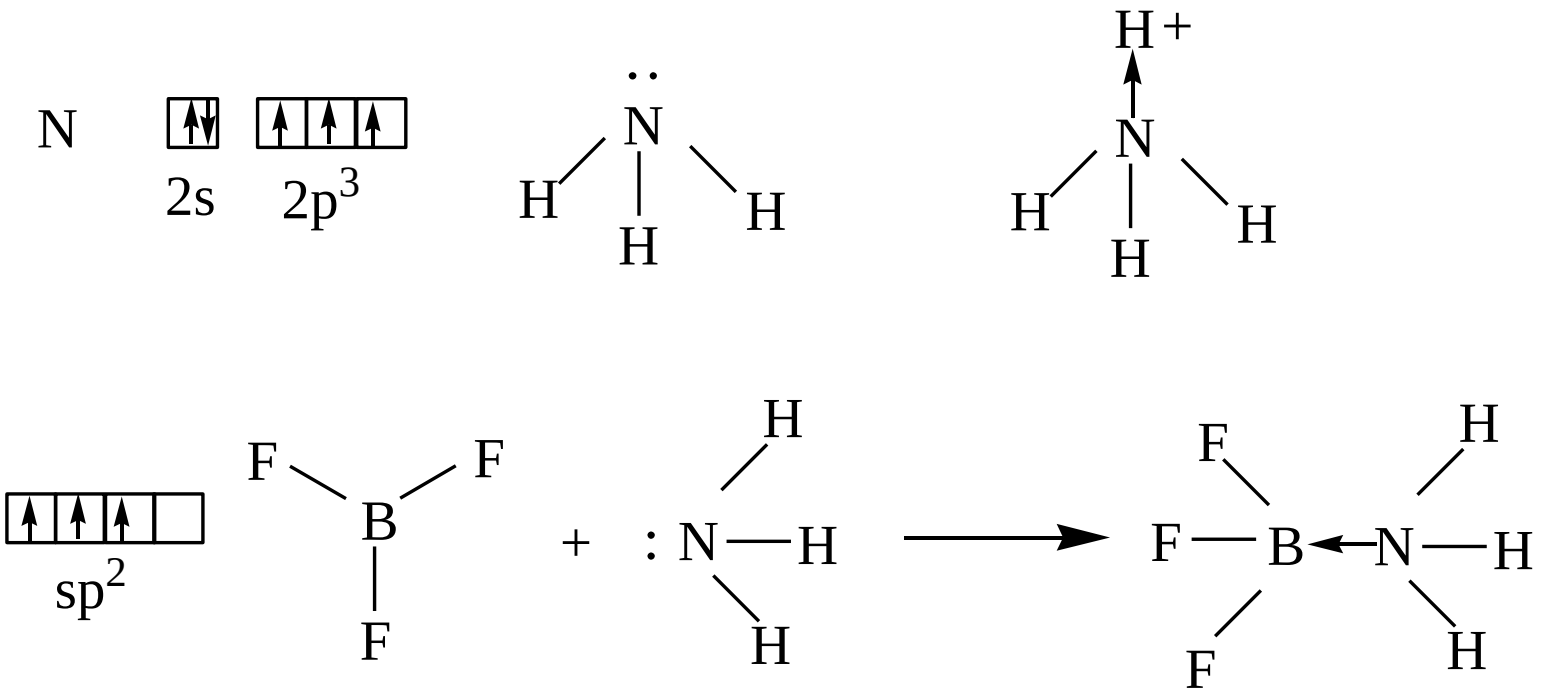
$OH^-$ = IONE OSSIDRILE

$H_2O$ = anfolita

$$NaOH \rightarrow Na^+ + OH^-$$

LEWIS

ACIDO ⇨ SPECIE CAPACE DI ACCETTARE LONE PAIRS
BASE ⇨ SPECIE CAPACE DI DONARE LONE PAIRS



$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$ ⟸ Reazione di autoprotolisi

base1 acido2 acido1 base2

$2\ H_2O \leftrightarrows H_3O^+ + OH^-$

$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$ $[H_2O]$=55,55 M = costante

$K_W = [H_3O^+][OH^-] = 10^{-14}$ ⟸ Costante di autoprotolisi
Prodotto ionico

Acqua neutra $[H_3O^+] = [OH^-] = x$ ⇨ $K_W = x^2 = 10^{-14}$

$\rightarrow x = [H_3O^+] = [OH^-] = \sqrt{K_W} = \sqrt{10^{-14}} = 10^{-7}$ M

$K_W = [H_3O^+][OH^-] = 10^{-14}$

pH+pOH=14

$pH = -\log [H_3O^+]$ $pOH = -\log [OH^-]$

Acqua neutra $[H_3O^+] = [OH^-] = 10^{-7}$ M ⇨ $pH = -\log [H_3O^+] = -\log 10^{-7} = 7$ $pOH = -\log [OH^-] = 7$

Soluzione acida $[H_3O^+] > [OH^-]$ $[H_3O^+] > 10^{-7}$ M ⇨ $pH = -\log [H_3O^+] < 7$

$HA + H_2O \leftrightarrows A^- + H_3O^+$ $[OH^-] < 10^{-7}$ M ⇨ $pOH = -\log [OH^-] > 7$

Soluzione basica $[OH^-] > [H_3O^+]$ $[H_3O^+] < 10^{-7}$ M ⇨ $pH = -\log [H_3O^+] > 7$

$B + H_2O \leftrightarrows OH^- + BH^+$ $[OH^-] > 10^{-7}$ M ⇨ $pOH = -\log [OH^-] < 7$

$pH = -\log [H_3O^+]$ ➡ $[H_3O^+] = 10^{-pH}$

$pOH = -\log [OH^-]$ ➡ $[OH^-] = 10^{-pOH}$

$K_W = [H_3O^+][OH^-] = 10^{-14}$ ➡ $pH + pOH = 14$

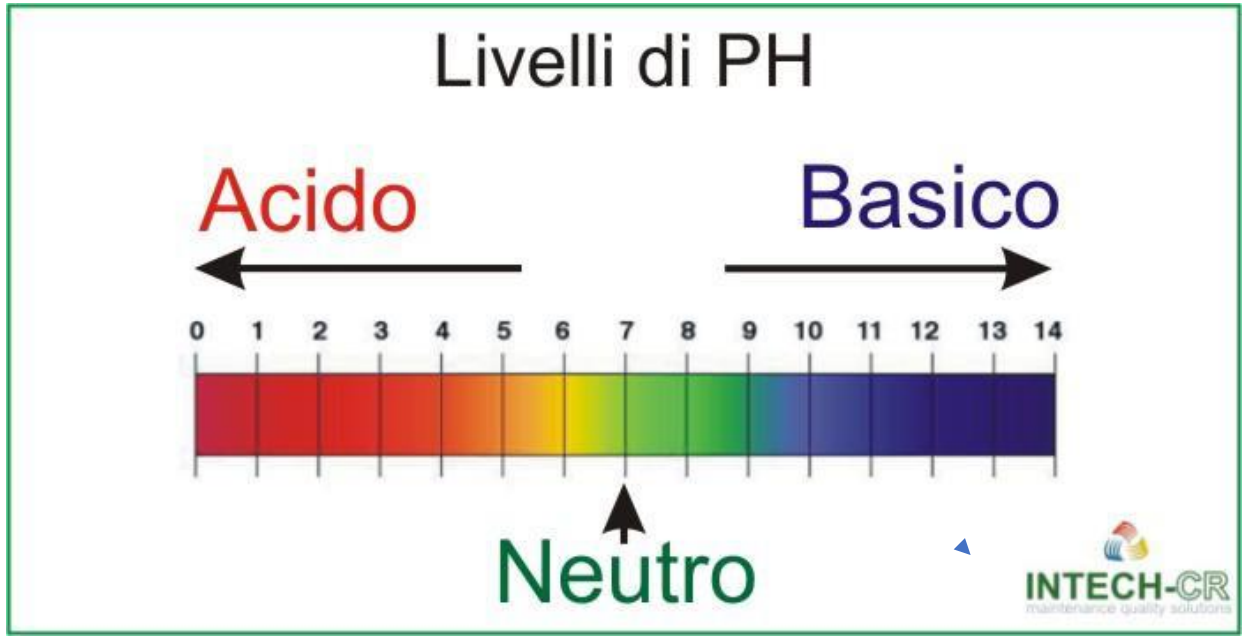
$0 \leq pH \leq 14$

$1\ M \geq [H_3O^+] \geq 10^{-14}\ M$

Acqua neutra:

$[H_3O^+] = [OH^-] = 10^{-7}\ M$

$pH = pOH = 7$




Soluzione acida $[H_3O^+] > [OH^-]$

$[H_3O^+] > 10^{-7}\ M$ ⇨ $pH < 7$

$[OH^-] < 10^{-7}\ M$ ⇨ $pOH > 7$

Soluzione basica $[OH^-] > [H_3O^+]$

$[H_3O^+] < 10^{-7}\ M$ ⇨ $pH > 7$

$[OH^-] > 10^{-7}\ M$ ⇨ $pOH < 7$

$14 \geq pOH \geq 0$

$10^{-14} \leq [OH^-] \leq 1\ M$

# Acidi e basi

ACIDI FORTI

$HA + H_2O \rightarrow A^- + H_3O^+$

Es. $HCl + H_2O \rightarrow Cl^- + H_3O^+$

ACIDI DEBOLI

$HA + H_2O \leftrightarrows A^- + H_3O^+$ ← $K_a = \dfrac{[A^-][H_3O^+]}{[HA]}$

$HF + H_2O \leftrightarrows F^- + H_3O^+$ ← $K_a = \dfrac{[F^-][H_3O^+]}{[HF]} = 6{,}6 \times 10^{-4}$

BASI FORTI

$NaOH \rightarrow Na^+ + OH^-$ ← MONOPROTICA

$Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^-$ ← DIPROTICA

BASI DEBOLI

$B + H_2O \leftrightarrows BH^+ + OH^-$ ← $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ ← $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = 1{,}8 \times 10^{-5}$

# CALCOLO DEL pH

Acido forte: HCl c= 0,1 M pH = ?

$HCl + H_2O \rightarrow Cl^- + H_3O^+$

c $\rightarrow$ c c

$[H_3O^+]$ = c= 0,1 M = $10^{-1}$ M pH = - log $[H_3O^+]$ = 1

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Base forte: NaOH c= 0,1 M pH = ?

$NaOH \rightarrow Na^+ + OH^-$

c $\rightarrow$ c c

$[OH^-]$ = c = 0,1 M = $10^{-1}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}\,M \qquad pH = -\log [H_3O^+] = 13$$

pOH = -log $[OH^-]$ = 1 pH=14-pOH=13

ACIDO DEBOLE

HCN c= 0,1 M $K_a$= 6,2 x $10^{-10}$

$$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$$
$$c\text{-}x \qquad\qquad x \qquad\quad x$$

$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{x^2}{c-x} \simeq \frac{x^2}{c}$$

$x << c \rightarrow c\text{-}x \simeq c$

$K_a < 10^{-3}$ $\quad c > 10^{-3}$ M

$$[H_3O^+] = x = \sqrt{K_a \times c} = \sqrt{6{,}2 \times 10^{-10} \times 0{,}1} = 7{,}8\ x10^{-6}\ M$$

$$pH = -\log [H_3O^+] = -\log(7{,}8\ x10^{-6}) = 5{,}1$$

# Grado di dissociazione

$$\alpha = \frac{\text{n.dissociate}}{\text{n.iniziali}} \qquad 0 \leq \alpha \leq 1$$

$$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$$

| | | |
|---|---|---|
| 1-α | α | α |
| c(1-α) | αc | αc |

$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{(\alpha c)^2}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha} \simeq \alpha^2 c$$

$$\alpha << 1 \rightarrow 1 - \alpha \simeq 1$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{6{,}2\times10^{-10}}{0{,}1}} = 7{,}8\ x10-5$$

$$\alpha = \frac{[H_3O^+]}{c} = \frac{7{,}8\times10^{-6}}{0{,}1} = 7{,}8\ x10^{-5}$$

BASE DEBOLE $NH_3$ $c=0,1\ M$ $K_b= 1,8 \times 10^{-5}$

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$
$$c-x \qquad\qquad x \quad x$$

$$K_b=\frac{[NH_4^+][OH^-]}{[NH_3]}=\frac{x^2}{c-x}\simeq\frac{x^2}{c}$$

$x<<c \rightarrow c-x\simeq c$

$K_b<10^{-3}$ $c>10^{-3}\ M$

$$[OH^-]=x=\sqrt{K_b \times c}=\sqrt{1,8\times10^{-5}\times0,1}=1,34\ x10^{-3}\ M$$

$$pOH = -\log [OH^-] = -\log (1,34 \times 10^{-3}) = 2,87$$

$$pH = 14 - pOH = 11,13$$

$$[H_3O^+]=\frac{K_w}{[OH^-]}=\frac{10^{-14}}{1,34\times10^{-3}}=7,5 \times 10^{-12}\ M$$

$$pH = -\log [H_3O^+] = -\log (7,5\ x10^{-12}) = 11,13$$

# ACIDI POLIPROTICI

$$H_2S + H_2O \leftrightarrows HS^- + H_3O^+ \qquad K_{a1} = \frac{[HS^-][H_3O^+]}{[H_2S]} = 10^{-7}$$

$$K_{a1} >> K_{a2}$$

$$HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+ \qquad K_{a2} = \frac{[S^{2-}][H_3O^+]}{[HS^-]} = 1{,}3 \times 10^{-14}$$

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$$H_3PO_4 + H_2O \leftrightarrows H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$$

$$H_2PO_4^- + H_2O \leftrightarrows HPO_4^{2-} + H_3O^+ \qquad K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$

$$HPO_4^{2-} + H_2O \leftrightarrows PO_4^{3-} + H_3O^+ \qquad K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]}$$

$$K_{a1} > K_{a2} > K_{a3}$$

# FATTORI CHE INFLUENZANO LA FORZA DEGLI ACIDI E DELLE BASI

ACIDI X-H LUNGO IL PERIODO $LiH < BeH_2 < CH_4 < NH_3 < H_2O < HF$

CARATTERE ACIDO →

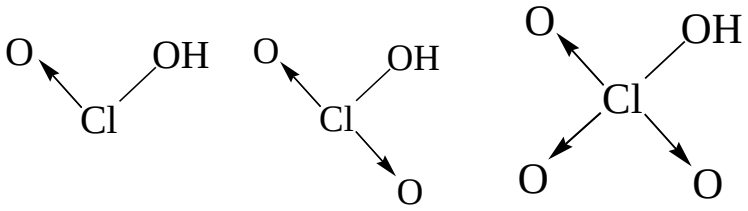
LUNGO IL GRUPPO $H_2O < H_2S < H_2Se < H_2Te$ $HF < HCl < HBr < HI$

OSSIACIDI: $HIO < HBrO < HClO$ $I\text{-}O\text{-}H < Br\text{-}O\text{-}H < Cl\text{-}O\text{-}H$

(+1) (+3) (+5) (+7)

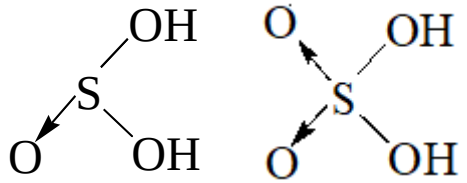
$HClO < HClO_2 < HClO_3 < HClO_4$

Cl-OH




(+4) (+6)

$H_2SO_3 < H_2SO_4$

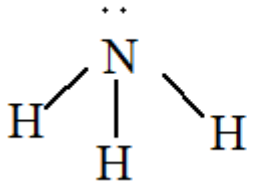


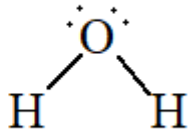

$H_2SO_3 \leftrightarrows H^+ + HSO_3^-$

$HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$

BASI FORTI $NaOH \rightarrow Na^+ + OH^-$

BASI DEBOLI $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$




CARATTERE BASICO: $NH_3 > H_2O > HF$

# SOSTANZE ANFOTERE - ANFOLITI

$Al(OH)_3 + 3\ H_3O^+ \leftrightarrows Al^{3+} + 6\ H_2O$

$Al(OH)_3 + OH^- \leftrightarrows Al(OH)_4^- \leftrightarrows AlO_2^- + 2\ H_2O$

$H_2O + NH_3 \leftrightarrows NH_4^+ + OH^-$

$H_2O + HCl \rightarrow Cl^- + H_3O^+$

$H_2PO_4^- + H_3O^+ \rightarrow H_3PO_4 + H_2O$

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

$NH_2\text{-}R\text{-}COOH$ AMINOACIDI

$NH_2\text{-}R\text{-}COOH + OH^- \rightarrow NH_2\text{-}R\text{-}COO^- + H_2O$

$NH_2\text{-}R\text{-}COOH + H_3O^+ \rightarrow NH_3^+\text{-}R\text{-}COOH + H_2O$

✸ $HNO_2 + H_2O \leftrightarrows NO_2^- + H_3O^+$

acido1 base2 base1 acido2

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

$NaNO_2 \rightarrow Na^+ + NO_2^-$

❋ $NO_2^- + H_2O \leftrightarrows HNO_2 + OH^-$

base1 acido2 acido1 base2

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

Lo ione $NO_2^-$ è la base coniugata dell'acido $HNO_2$

$$K_a \times K_b = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} \times \frac{[HNO_2][OH^-]}{[NO_2^-]} = [H_3O^+][OH^-] = K_W$$

$K_a x K_b = K_W$ $\quad K_b = \frac{K_W}{K_a}$ $\quad K_a = \frac{K_W}{K_b}$

# IDROLISI SALINA

$NaNO_2 \rightarrow$ deriva da → $NaOH$ = base forte

$HNO_2$ = acido debole

$NaNO_2 \rightarrow Na^+ + NO_2^-$

$NO_2^- + H_2O \leftrightarrows HNO_2 + OH^-$

$K_i = K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = \frac{K_W}{K_a}$

pH basico

~~$Na^+ + H_2O \leftrightarrows NaOH + H^+$~~

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$NH_4Cl \rightarrow$ deriva da → $NH_3$ = base debole

HCl = acido forte

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

$K_i = K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_W}{K_b}$

pH acido

| base | acido | reazione | sale | catione | anione | idrolisi | $K_i$= | pH |
|---|---|---|---|---|---|---|---|---|
| forte | forte | | | | | | | |
| NaOH | + HCl | $\rightarrow NaCl + H_2O$ | NaCl | $\rightarrow Na^+$ | $+ Cl^-$ | / | / | neutra |
| forte | debole | | | | basico | | | |
| NaOH | $+ HNO_2$ | $\rightarrow NaNO_2 + H_2O$ | $NaNO_2$ | $\rightarrow Na^+$ | $+ NO_2^-$ | $NO_2^- + H_2O \rightleftarrows HNO_2 + OH^-$ | $K_i=K_b=\frac{K_w}{K_a}$ | basica |
| debole | forte | | | acido | | | | |
| $NH_3$ | + HCl | $\rightarrow NH_4Cl$ | $NH_4Cl$ | $\rightarrow NH_4^+$ | $+ Cl^-$ | $NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$ | $K_i=K_a=\frac{K_w}{K_b}$ | acida |
| debole | debole | | | acido | basico | | | |
| $NH_3$ | $+ HNO_2$ | $\rightarrow NH_4NO_2$ | $NH_4NO_2$ | $\rightarrow NH_4^+$ | $+ NO_2^-$ | $NO_2^- + H_2O \rightleftarrows HNO_2 + OH^-$<br>$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$ | $K_i=K_b=\frac{K_w}{K_a}$<br>$K_i=K_a=\frac{K_w}{K_b}$ | ? |

SOLUZIONE TAMPONE → Si oppone a variazioni di pH

ACIDO DEBOLE (HA) + un suo SALE con BASE FORTE (NaA) $NaOH+HA \rightarrow NaA+H_2O$

Es. HF + NaF, $HNO_2$ + $NaNO_2$

$HA + H_2O \leftrightarrows A^- + H_3O^+$ dissociazione acido: parziale

$NaA \rightarrow Na^+ + A^-$ dissociazione sale: totale

$c_S$

$c_A$= conc. dell'acido

$c_S$= conc. del sale

$HA + H_2O \leftrightarrows A^- + H_3O^+$

$c_A$ $c_S$

$[HA] = c_A$

$[A^-]=c_S$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \Rightarrow [H_3O^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \times \frac{c_A}{c_S}$$

$$pH = -\log[H_3O^+] = -\log\left(K_a \frac{c_A}{c_S}\right) = -\log K_a - \log\frac{c_A}{c_S} = pK_a + \log\frac{c_S}{c_A}$$

$$pH = pK_a + \log\frac{c_S}{c_A}$$

$c_S = c_A$ $pH = pK_a$

# SOLUZIONE TAMPONE

$$pH = pK_a + \log \frac{c_S}{c_A}$$

Aggiungiamo $c_H$ moli/l di un acido forte HCl ($c_H << c_S, c_A$)

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$
$$c_H$$

$$A^- + H_3O^+ \rightarrow HA + H_2O$$
$$c_S \quad c_H \quad c_A$$
$$c_S - c_H \quad c_A + c_H$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(c_S - c_H)[H_3O^+]}{(c_A + c_H)}$$

$$[H_3O^+] = K_a \times \frac{(c_A + c_H)}{(c_S - c_H)}$$

$$pH = pK_a + \log \frac{c_S - c_H}{c_A + c_H} \simeq pK_a + \log \frac{c_S}{c_A}$$

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Aggiungiamo $c_{OH}$ moli/l di una base forte NaOH ($c_{OH} << c_S, c_A$)

$$NaOH \rightarrow Na^+ + OH^-$$
$$c_{OH}$$

$$HA + OH^- \rightarrow A^- + H_2O$$
$$c_A \quad c_{OH} \quad c_S$$
$$c_A - c_{OH} \quad c_S + c_{OH}$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(c_S + c_{OH})[H_3O^+]}{(c_A - c_{OH})}$$

$$[H_3O^+] = K_a \frac{(c_A - c_{OH})}{(c_S + c_{OH})}$$

$$pH = pK_a + \log \frac{c_S + c_{OH}}{c_A - c_{OH}} \simeq pK_a + \log \frac{c_S}{c_A}$$

BASE DEBOLE B ($c_B$)
+ suo SALE con ACIDO FORTE BHCl ($c_S$)

$B + HCl \rightarrow BHCl$
Es. $NH_3 + NH_4Cl$

$$BHCl \rightarrow BH^+ + Cl^-$$
$$c_S$$

$$B + H_2O \leftrightarrows BH^+ + OH^-$$
$$c_B \qquad c_S$$

$[B] = c_B$
$[BH^+] = c_S$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad \Rightarrow \quad [OH^-] = K_b \frac{[B]}{[BH^+]} = K_b \frac{c_B}{c_S}$$

$$pOH = -\log [OH^-] = pK_b + \log \frac{c_S}{c_B}$$