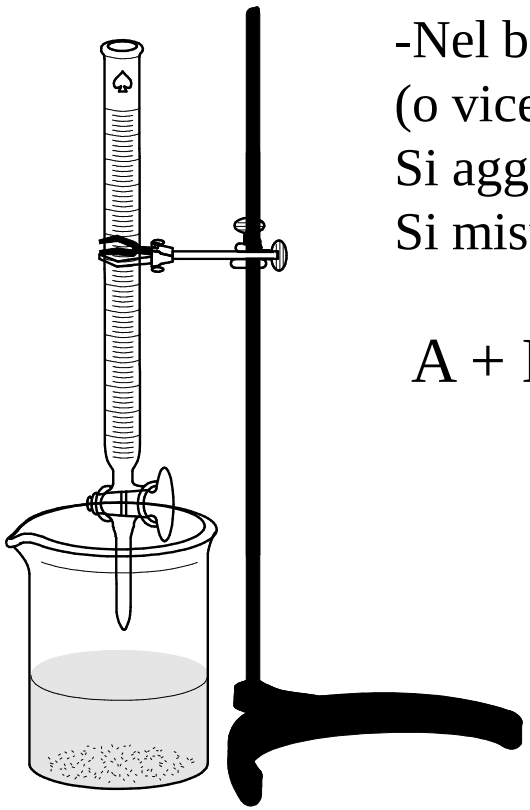
TITOLAZIONI

Determinazione della concentrazione di una soluzione a titolo incognito mediante reazione con una soluzione a titolo noto.



-Nella buretta: soluzione (B) a titolo noto (M_B)
-Nel becher: volume noto (V_A) di soluz. A da titolare (M_A) (o viceversa)
Si aggiunge sol. B a sol. A fino al punto di equivalenza
Si misura V_B all'equivalenza

$$n_A = n_B$$

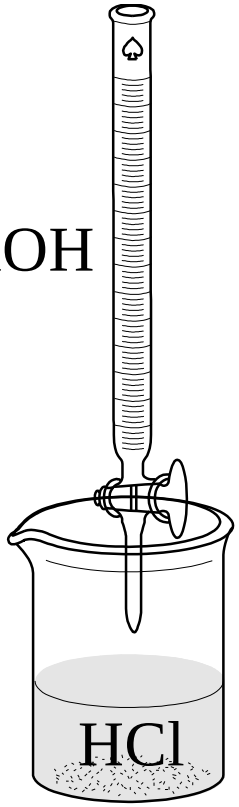
$$A + B \rightarrow \text{prodotti} \qquad M_A V_A = M_B V_B$$

Reazione: deve essere quantitativa, veloce, a stechiometria definita

Determinazione punto di equivalenza:
- Mediante indicatori;

TITOLAZIONI ACIDO-BASE

ACIDO FORTE - BASE FORTE

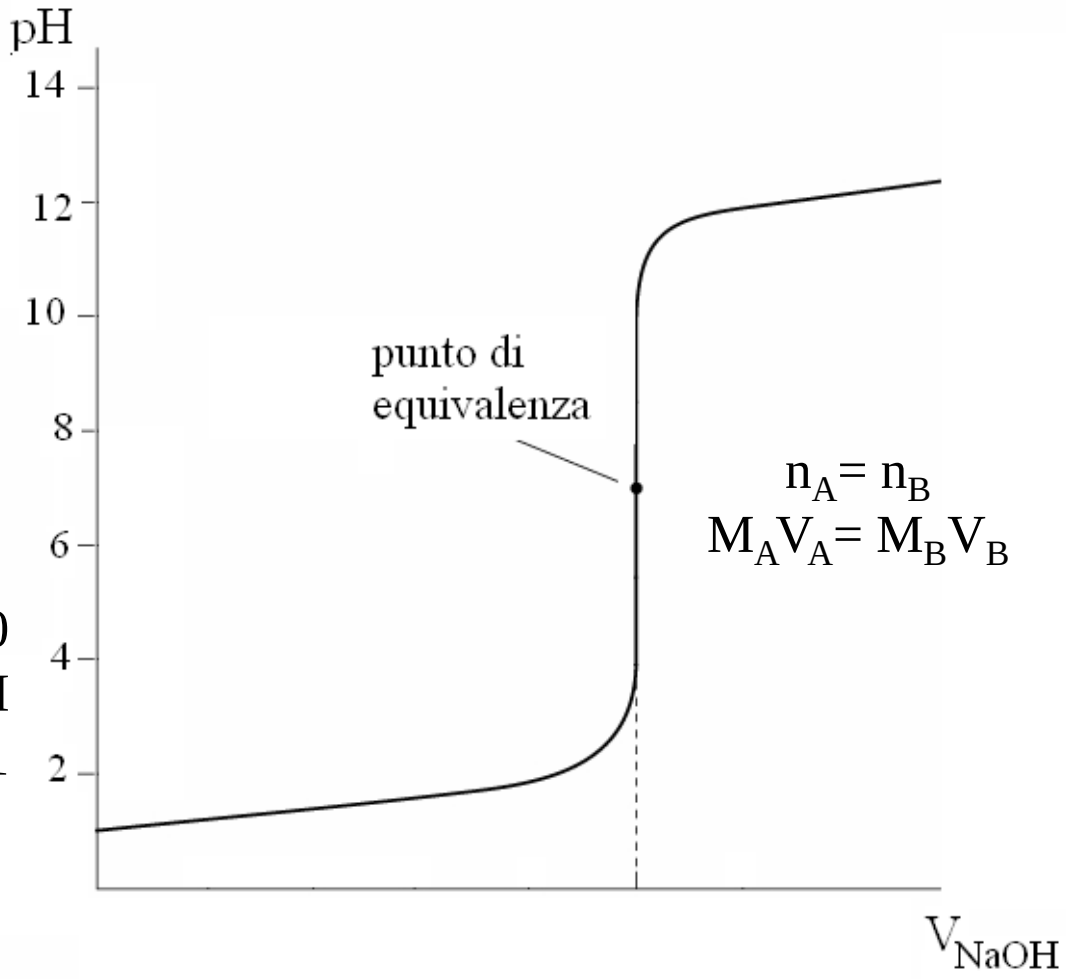


HCl 0,1 M

$V_B = 0$

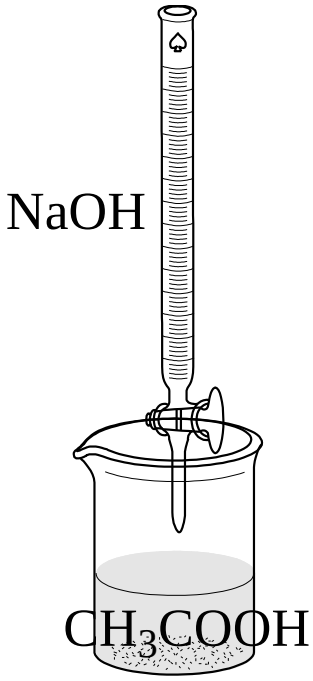
$[H_3O^+] = 0{,}1$ M

$pH = -\log [H_3O^+] = 1$



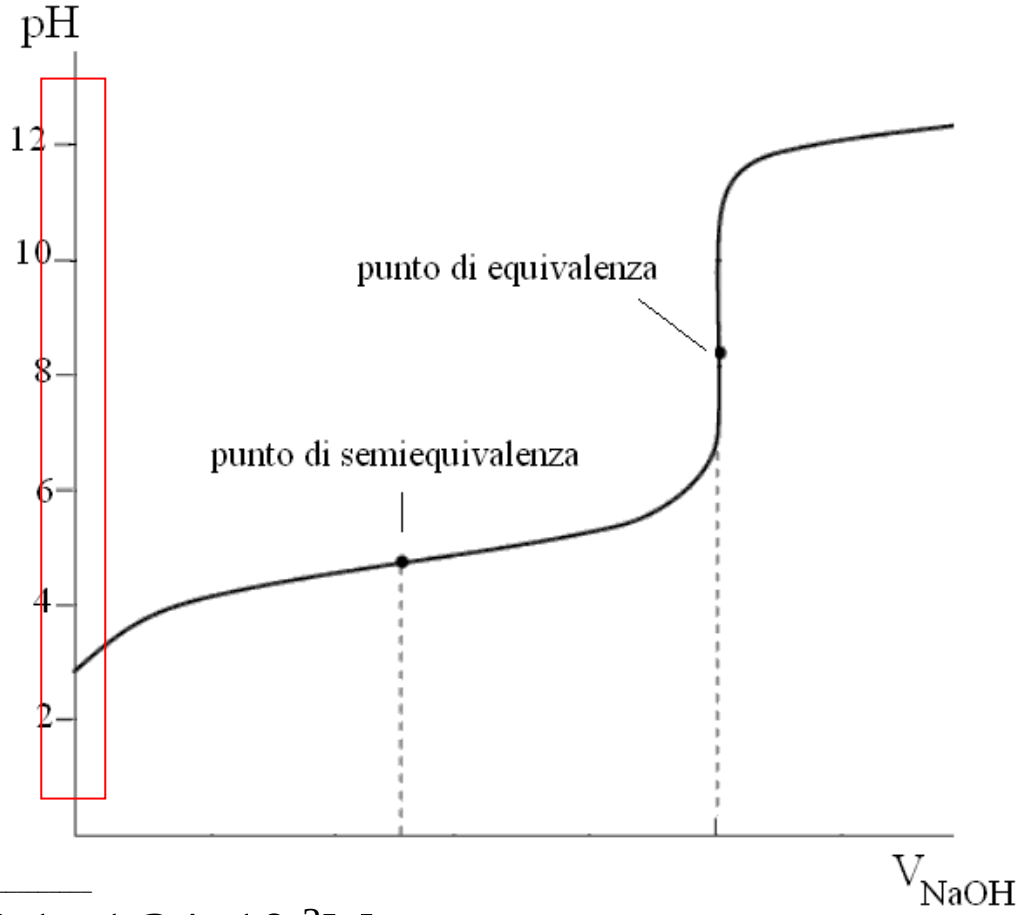
$HCl + NaOH \rightarrow NaCl + H_2O$

ACIDO DEBOLE - BASE FORTE



$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

CH_3COOH
0,10 M = c
$K_a = 1{,}8 \times 10^{-5}$
NaOH ~0,1 M



$CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$

c-x ~ c x x

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{c}$$

$[H_3O^+] = x = \sqrt{K_a x c} = \sqrt{1{,}8 \times 10^{-5} \times 0{,}1} = 1{,}34 \times 10^{-3} M$

$pH = -\log[H_3O^+] = 2{,}9$

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

⇨ Si forma una soluzione tampone

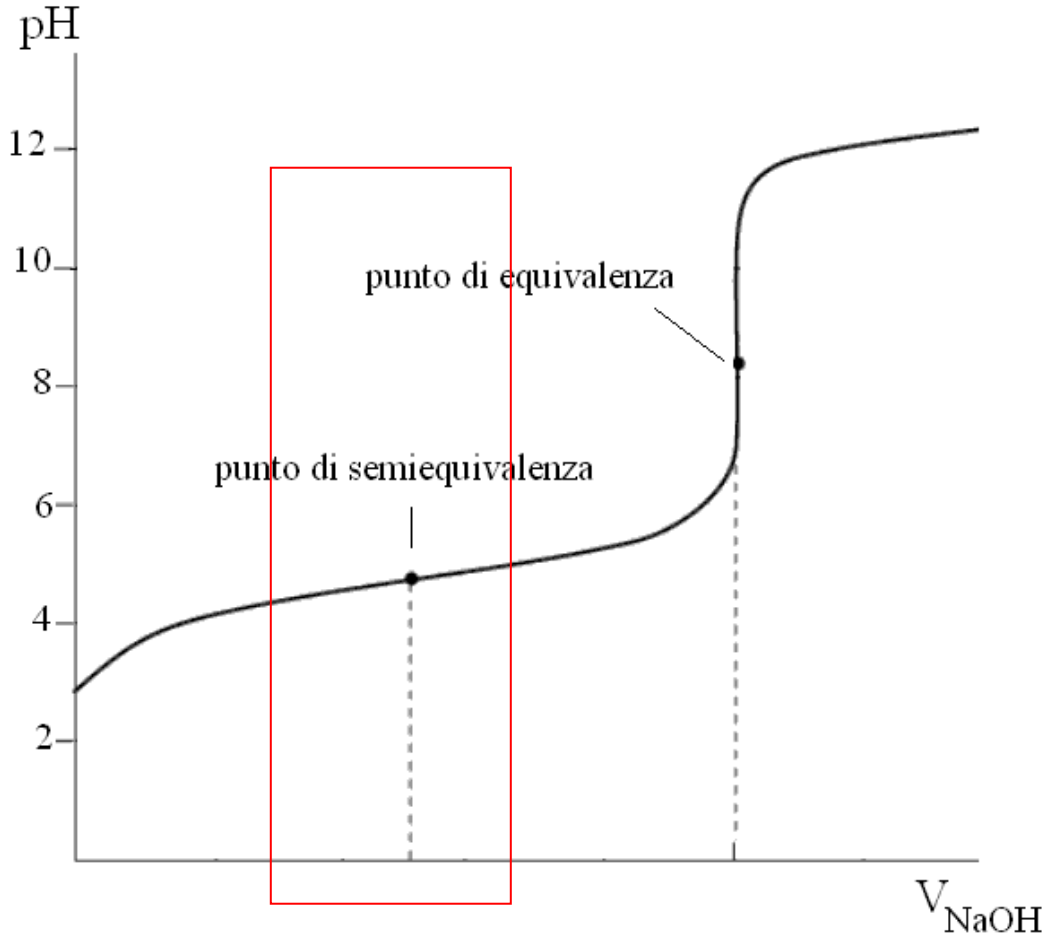
$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{c_S[H_3O^+]}{c_A}$$

$[CH_3COOH] = c_A$

$[CH_3COO^-] = c_S$

$$[H_3O^+] = K_a \frac{c_S}{c_A}$$

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



50% di titolante aggiunto

$c_A = c_S$ $pH = pK_a$

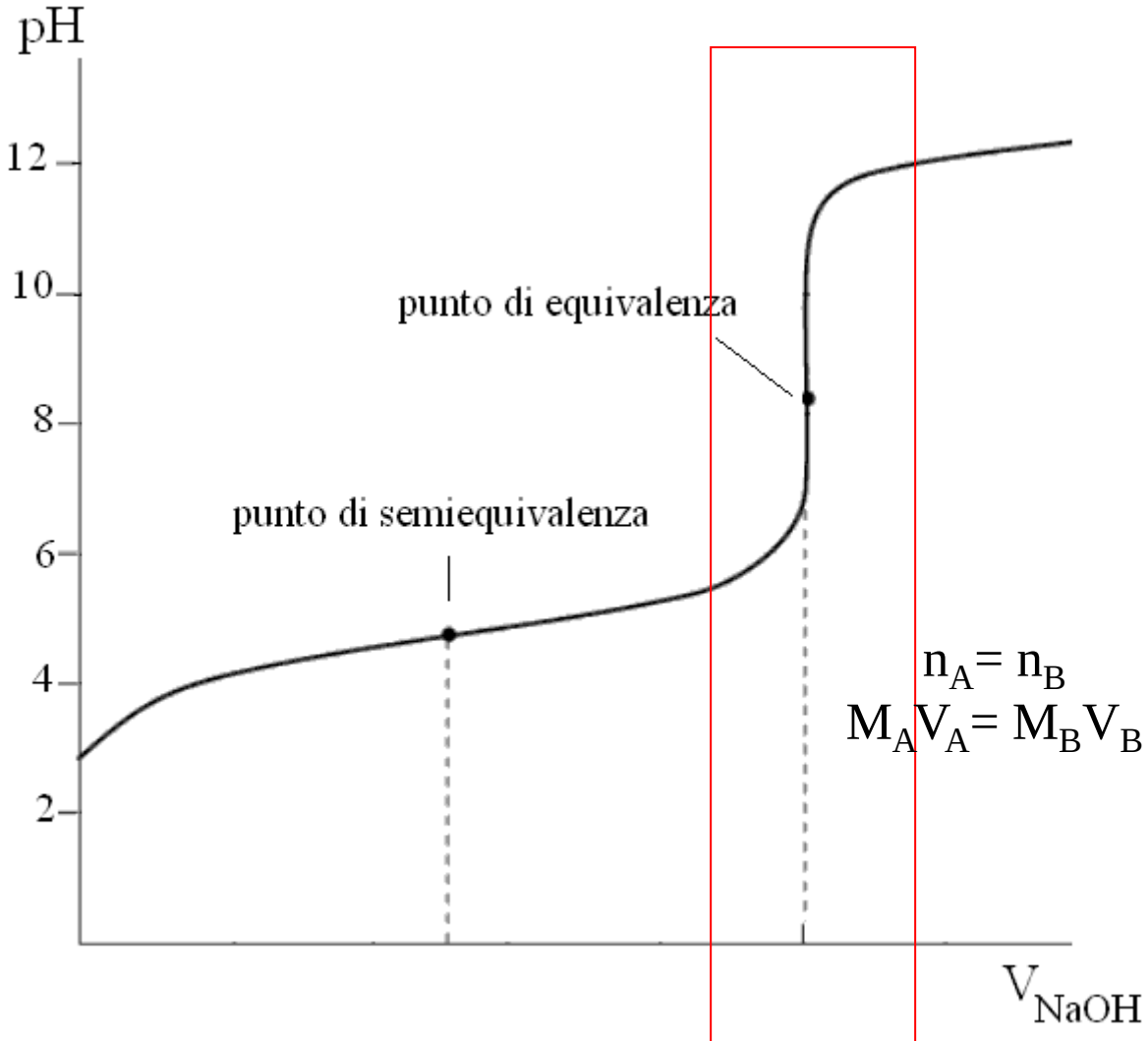
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$
$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

Punto di equivalenza

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$

$$K_i = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_i = \frac{K_w}{K_a} = \frac{10^{-14}}{1{,}8 \times 10^{-5}} = 5{,}5 \times 10^{-11}$$



$$n_A = n_B$$
$$M_A V_A = M_B V_B$$

Indicatori acido-base

$HInd + H_2O \leftrightarrows Ind^- + H_3O^+$

coloreA colore B

$$K_{Ind} = \frac{[Ind^-][H_3O^+]}{[HInd]}$$

$$[H_3O^+] = K_{Ind} \frac{[HInd]}{[Ind^-]} \Longrightarrow pH = pK_{Ind} + \log \frac{[Ind^-]}{[HInd]}$$

Col. A $[HInd] >> [Ind^-]$ $pH < pK_{Ind} \Rightarrow [H_3O^+] > K_{ind}$

Col. B $[HInd] << [Ind^-]$ $pH > pK_{Ind} \Rightarrow [H_3O^+] < K_{ind}$

Viraggio: $[HInd] = [Ind^-]$ $pH = pK_{Ind} \Rightarrow [H_3O^+] = K_{ind}$

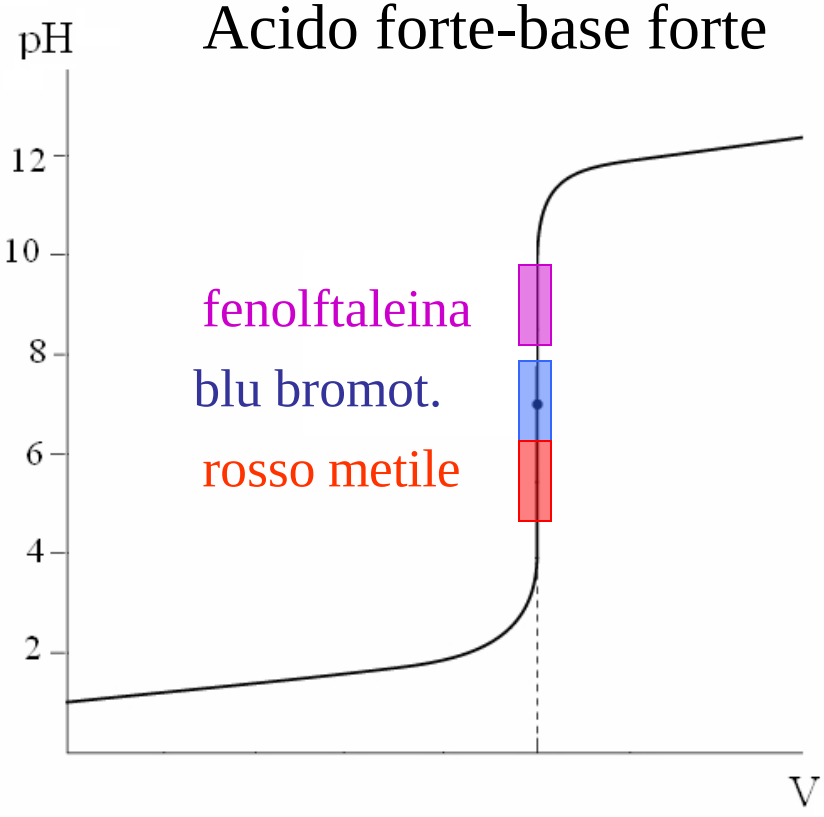
$[HInd] = 10[Ind^-]$ $pH = pK_{Ind} - 1$ colore A

$[Ind^-] = 10[HInd]$ $pH = pK_{Ind} + 1$ colore B

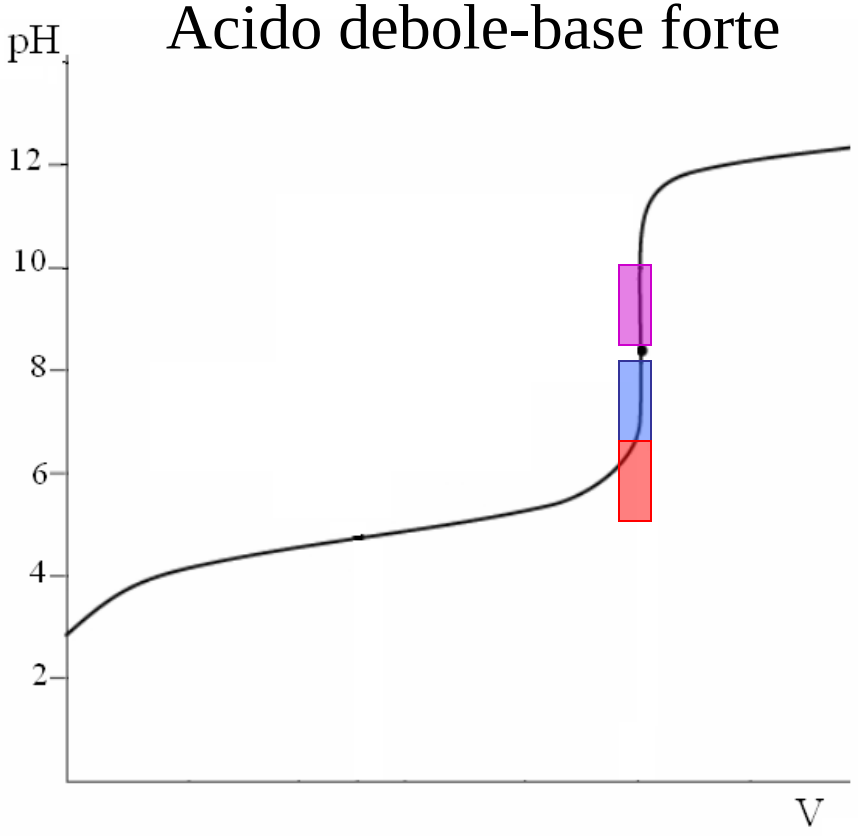
$pH = pK_{Ind} \pm 1$ intervallo di viraggio

Indicatore	pK_{Ind}	Intervallo	col. A	col. B
metilarancio	3,7	3,1 – 4,4	rosso	giallo
rosso metile	5,1	4,4 – 6,2	rosso	giallo
blu bromotimolo	7,0	6,2 – 7,6	giallo	blu
rosso fenolo	7,9	6,4 – 8,0	giallo	rosso
fenolftaleina	9,4	8,0 – 10,0	incolore	viola

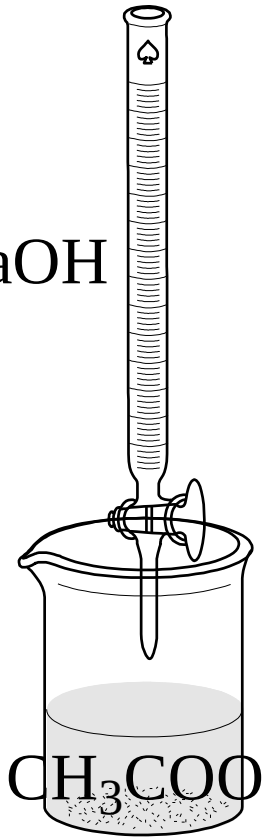
Acido forte-base forte



Acido debole-base forte



Esperienza 1
Titolazione dell'acido acetico contenuto in un campione di aceto



$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O$$

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Indicatore fenolftaleina

$n_A = n_B$ ⇒ $M_A V_A = M_B V_B$ ⇒ $M_A = \frac{M_B V_B}{V_A}$

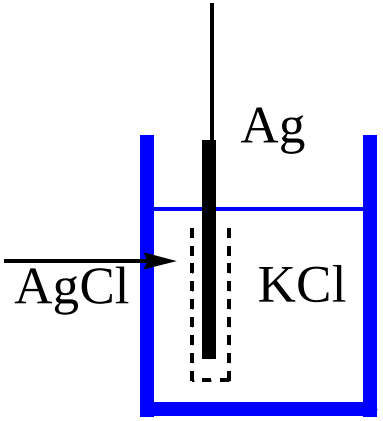
Potenziometria

Misura f.e.m. di una pila $E_{pila} = E_{mis} - E_{ref}$

Elettrodo di misura

Elettrodo di riferimento

Elettrodi di II specie $Ag \mid AgCl \mid KCl$



$Ag^+ + e^- \rightarrow Ag°$

$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$

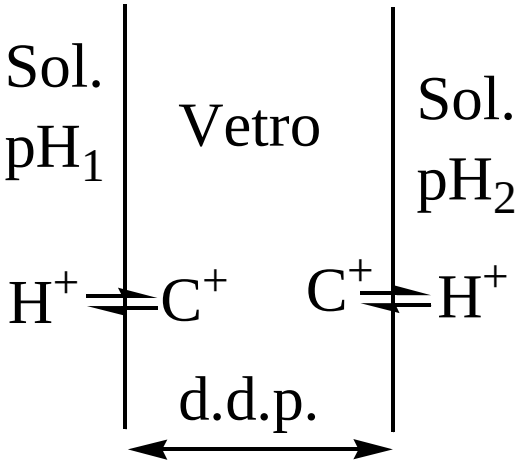
$K_{PS}=[Ag^+][Cl^-] \Rightarrow [Ag^+]= K_{PS}/[Cl^-]$

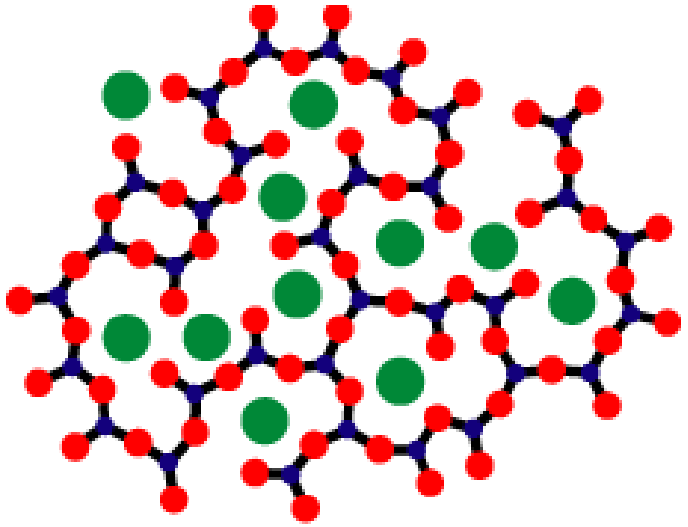
$E_{Ag^+/Ag} = E°_{Ag^+/Ag} + 0{,}059 \log [Ag^+] = E°_{Ag^+/Ag} + 0{,}059 \log(K_{PS}/[Cl^-])$

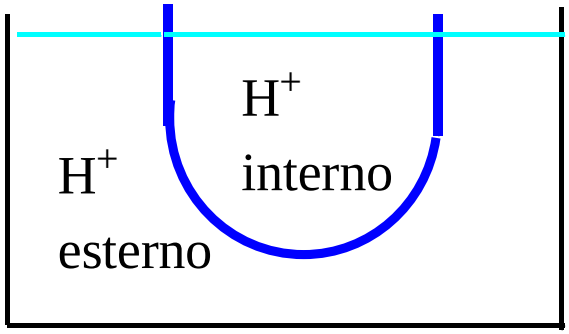
Elettrodi a membrana → scambio ionico

Elettrodo a vetro → H_3O^+

Vetro: tetraedri SiO_4







$$V = c \log \frac{[H^+]_{\text{int}}}{[H^+]_{est}}$$

pHmetro

Elettrodo a vetro

Membrana di vetro

$Ag_{(s)} \mid AgCl_{(s)} \mid Cl^-_{(aq)} \,||\, H^+_{(aq)\ est.} \,|\, H^+_{(aq)\ int}\ Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)}$

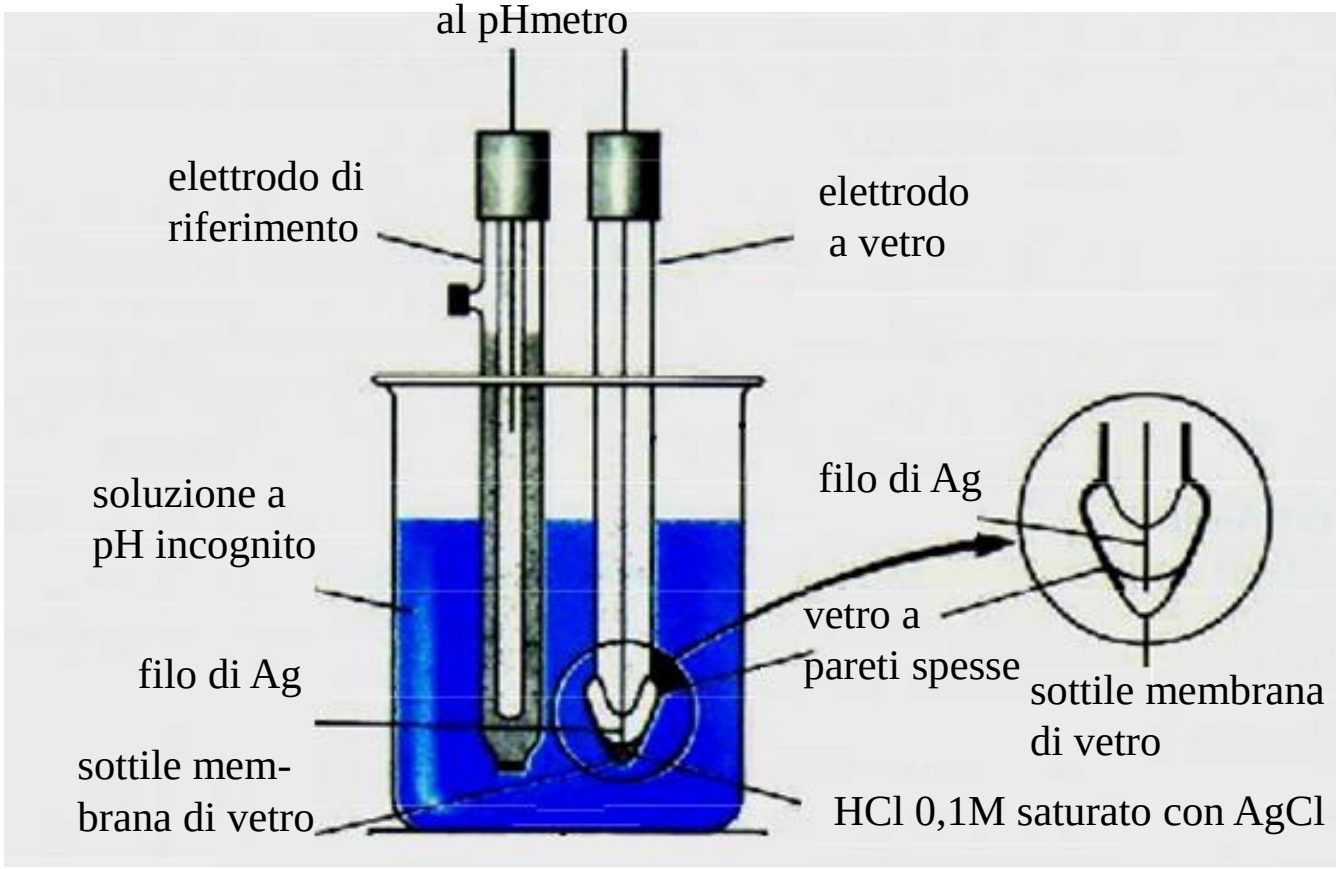
Elettrodo di riferimento

$[H^+]$ esterna (analita)

$[H^+]$ interno costante

Elettrodo di riferimento interno

$E = E^* + (cT)pH$



Seconda esperienza- Misure potenziometriche

Misura del pH di alcune soluzioni

Le misure di pH verranno effettuate tramite due diversi metodi:

a) Con il pHmetro
b) Con la cartina al tornasole

Preparazione di una soluzione tampone e verifica del potere tamponante.

Acido debole: acido acetico, CH_3COOH, ($Ka=1,8x10^{-5}$) +
Suo sale con base forte acetato di sodio, CH_3COONa