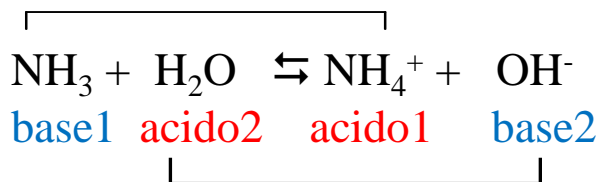
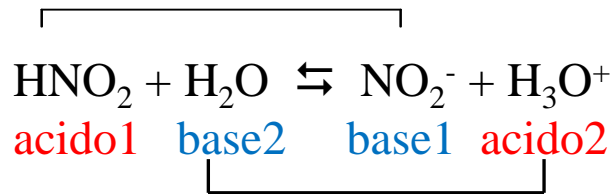
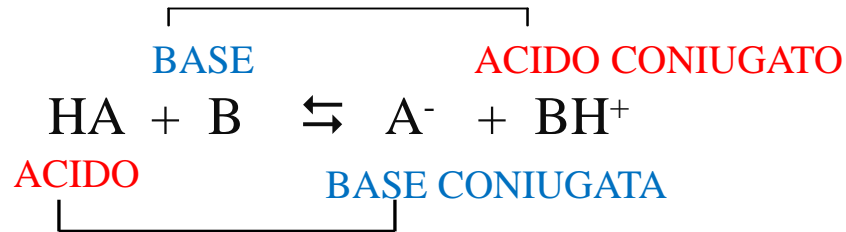


Reazioni acido base

BRÖNSTED E LOWRY

ACIDO \Rightarrow HA \Rightarrow SPECIE CAPACE DI DONARE IONI H⁺

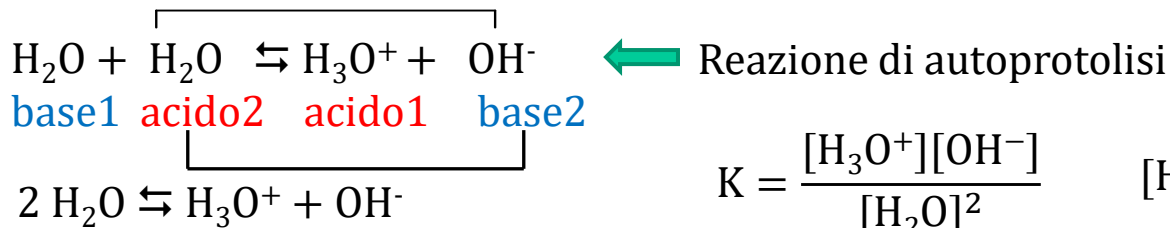
BASE \Rightarrow B \Rightarrow SPECIE CAPACE DI ACCETTARE IONI H⁺



H₃O⁺ = IONE IDROSSONIO
(OSSONIO)

OH⁻ = IONE OSSIDRILE

H₂O = anfotila



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad [\text{H}_2\text{O}] = 55,55 \text{ M} = \text{costante}$$

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

← Costante di autoprotolisi
Prodotto ionico

Acqua neutra $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x \quad \Rightarrow K_W = x^2 = 10^{-14}$

$$\rightarrow x = [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_W} = \sqrt{10^{-14}} = 10^{-7} \text{ M}$$

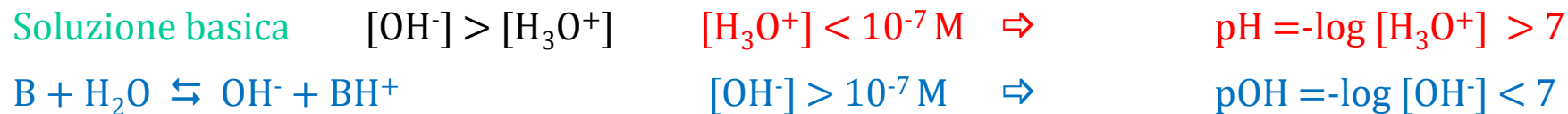
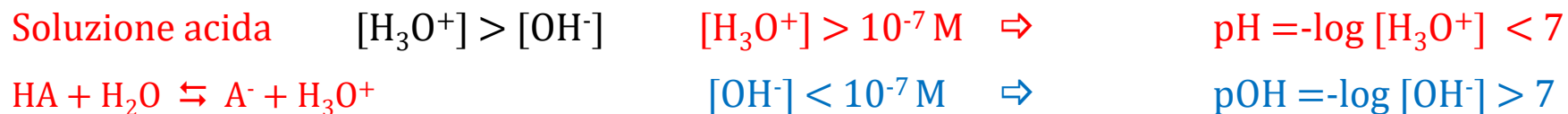
$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

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

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{Acqua neutra} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M} \Rightarrow \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 10^{-7} = 7 \quad \text{pOH} = -\log [\text{OH}^-] = 7$$



$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$



$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

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



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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$



$$\text{pH} + \text{pOH} = 14$$

$$0 \leq \text{pH} \leq 14$$

$$1 \text{ M} \geq [\text{H}_3\text{O}^+] \geq 10^{-14} \text{ M}$$

Acqua neutra:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

$$\text{pH} = \text{pOH} = 7$$

Soluzione acida $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

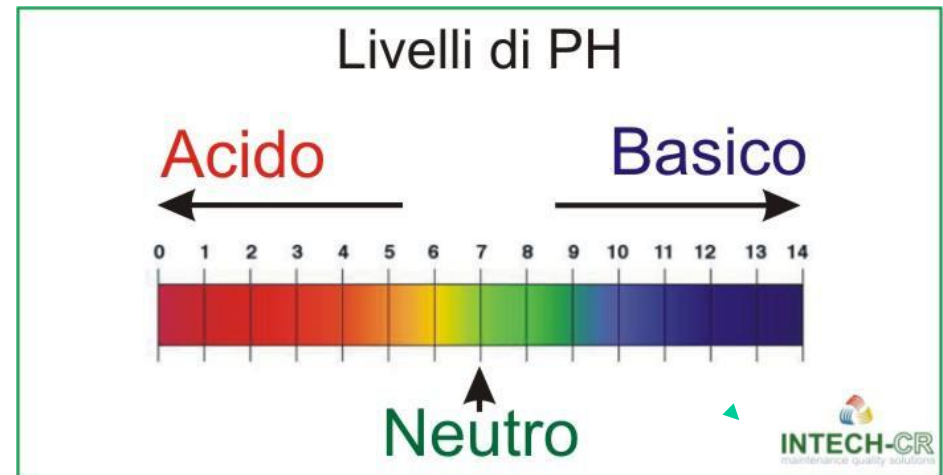
$$[\text{H}_3\text{O}^+] > 10^{-7} \text{ M} \Rightarrow \text{pH} < 7$$

$$[\text{OH}^-] < 10^{-7} \text{ M} \Rightarrow \text{pOH} > 7$$

Soluzione basica $[\text{OH}^-] > [\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] < 10^{-7} \text{ M} \Rightarrow \text{pH} > 7$$

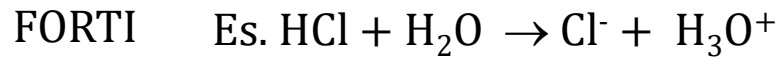
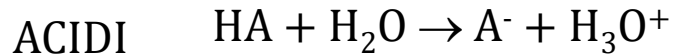
$$[\text{OH}^-] > 10^{-7} \text{ M} \Rightarrow \text{pOH} < 7$$



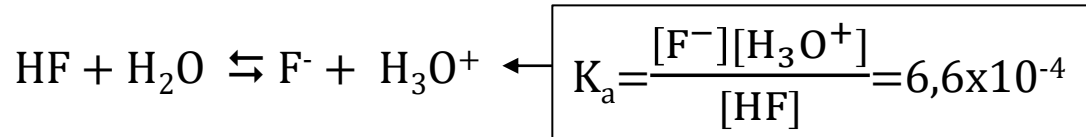
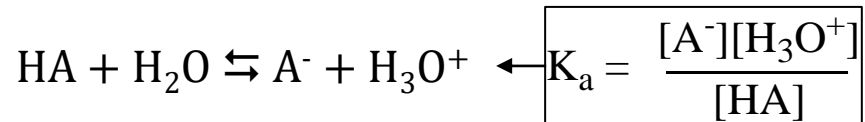
$$14 \geq \text{pOH} \geq 0$$

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

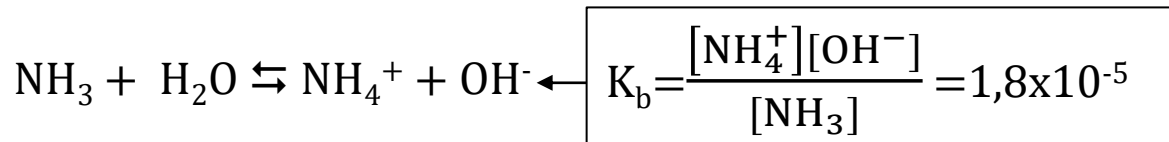
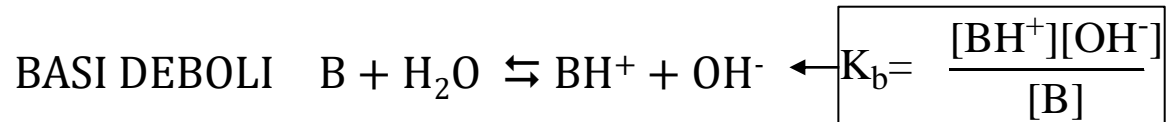
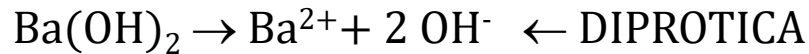
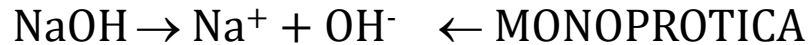
Acidi e basi



ACIDI
DEBOLI

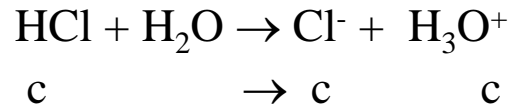


BASI FORTI



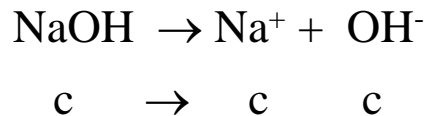
CALCOLO DEL pH

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



$$[\text{H}_3\text{O}^+] = c = 0,1 \text{ M} = 10^{-1} \text{ M} \qquad \text{pH} = -\log [\text{H}_3\text{O}^+] = 1$$

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



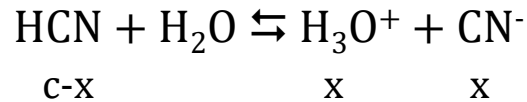
$$[\text{OH}^-] = c = 0,1 \text{ M} = 10^{-1} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13} \text{ M} \qquad \text{pH} = -\log [\text{H}_3\text{O}^+] = 13$$

$$\text{pOH} = -\log [\text{OH}^-] = 1 \qquad \text{pH} = 14 - \text{pOH} = 13$$

ACIDO DEBOLE

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



$$K_a = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} = \frac{x^2}{c-x} \approx \frac{x^2}{c}$$

$$x \ll c \rightarrow c-x \approx c$$

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

$$[\text{H}_3\text{O}^+] = x = \sqrt{K_a \times c} = \sqrt{6,2 \times 10^{-10} \times 0,1} = 7,8 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(7,8 \times 10^{-6}) = 5,1$$

BASE DEBOLE

NH₃

c=0,1 M K_b= 1,8 x10⁻⁵



$$x \ll c \rightarrow c-x \approx c$$

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

$$[\text{OH}^-] = x = \sqrt{K_b \times c} = \sqrt{1,8 \times 10^{-5} \times 0,1} = 1,34 \times 10^{-3} \text{ M}$$

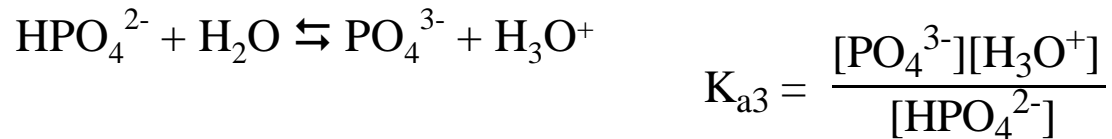
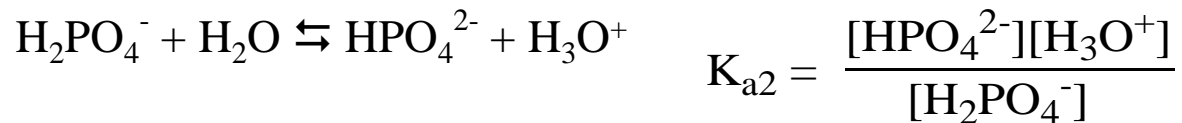
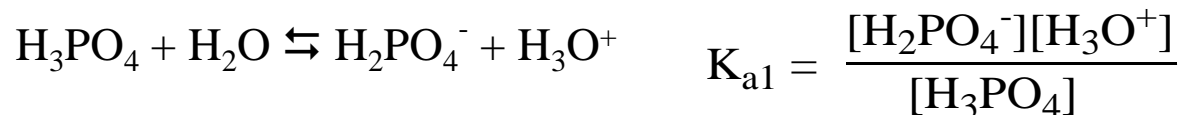
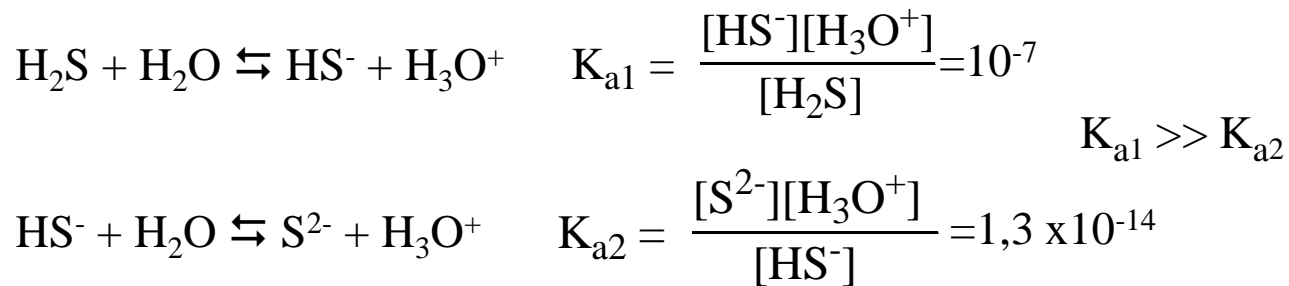
$$\text{pOH} = -\log [\text{OH}^-] = -\log (1,34 \times 10^{-3}) = 2,87$$

$$\text{pH} = 14 - \text{pOH} = 11,13$$

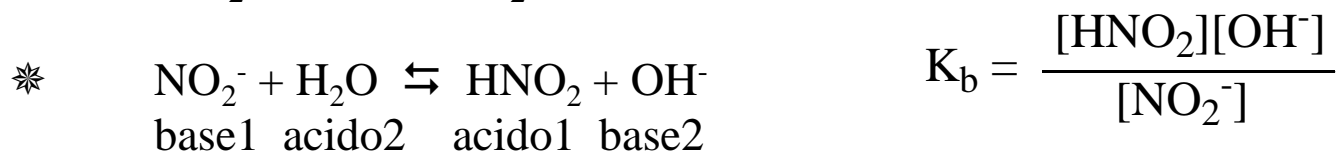
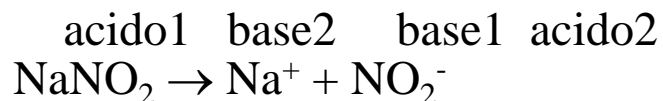
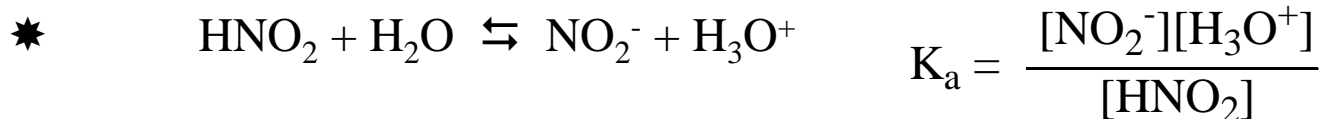
$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{1,34 \times 10^{-3}} = 7,5 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7,5 \times 10^{-12}) = 11,13$$

ACIDI POLIPROTICI



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



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

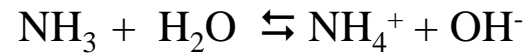
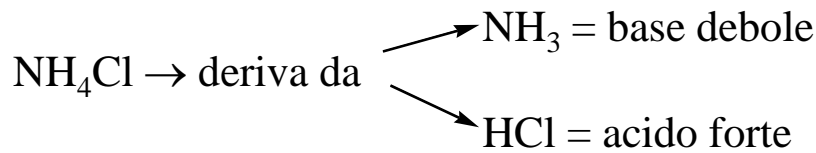
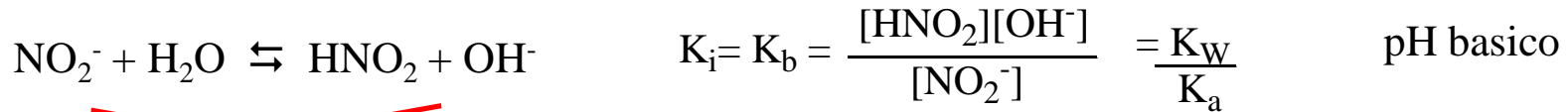
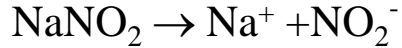
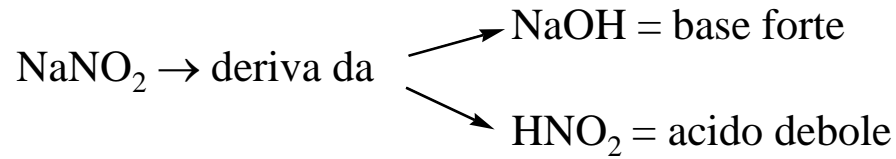
$$K_a \times K_b = \frac{[\cancel{\text{NO}_2^-}][\text{H}_3\text{O}^+]}{[\cancel{\text{HNO}_2}]} \times \frac{[\cancel{\text{HNO}_2}][\text{OH}^-]}{[\cancel{\text{NO}_2^-}]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

$$K_a \times K_b = K_w$$

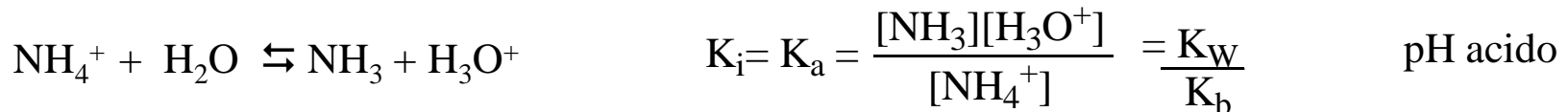
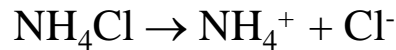
$$K_b = \frac{K_w}{K_a}$$

$$K_a = \frac{K_w}{K_b}$$

IDROLISI SALINA



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$



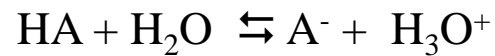
base	acido	reazione	sale	catione	anione	idrolisi	$K_i =$	pH
forte	forte							
NaOH	+ HCl	$\rightarrow \text{NaCl} + \text{H}_2\text{O}$	NaCl	$\rightarrow \text{Na}^+$	+ Cl^-	/	/	neutra
forte	debole				basico			
NaOH	+ HNO_2	$\rightarrow \text{NaNO}_2 + \text{H}_2\text{O}$	NaNO ₂	$\rightarrow \text{Na}^+$	+ NO_2^-	$\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$	$K_i = K_b = \frac{K_w}{K_a}$	basica
debole	forte			acido				
NH ₃	+ HCl	$\rightarrow \text{NH}_4\text{Cl}$	NH ₄ Cl	$\rightarrow \text{NH}_4^+$	+ Cl^-	$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$	$K_i = K_a = \frac{K_w}{K_b}$	acida
debole	debole			acido	basico			
NH ₃	+ HNO_2	$\rightarrow \text{NH}_4\text{NO}_2$	$\frac{\text{NH}_4\text{NO}_2}{2}$	$\rightarrow \text{NH}_4^+$	+ NO_2^-	$\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$	$K_i = K_b = \frac{K_w}{K_a}$ $K_i = K_a = \frac{K_w}{K_b}$?

SOLUZIONE TAMPONE

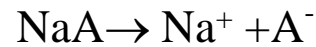


Si oppone a variazioni di pH

ACIDO DEBOLE (HA) + un suo SALE con BASE FORTE (NaA) NaOH+HA → NaA+H₂O
 Es. HF + NaF, HNO₂ + NaNO₂

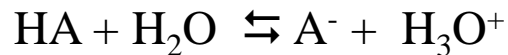


dissociazione acido: parziale $c_A = \text{conc. dell'acido}$



dissociazione sale: totale $c_S = \text{conc. del sale}$

c_S



$$[\text{HA}] = c_A$$

c_A

c_S

$$[\text{A}^-] = c_S$$

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \quad \Rightarrow \quad [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} = K_a \times \frac{c_A}{c_S}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(K_a \frac{c_A}{c_S}\right) = -\log K_a - \log \frac{c_A}{c_S} = \text{p}K_a + \log \frac{c_S}{c_A}$$

$$\text{pH} = \text{p}K_a + \log \frac{c_S}{c_A}$$

$$c_S = c_A$$

$$\text{pH} = \text{p}K_a$$

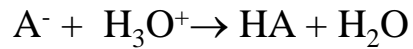
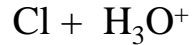
SOLUZIONE TAMPONE



$$\text{pH} = \text{pK}_a + \log \frac{c_S}{c_A}$$

Aggiungiamo c_H moli/l di un acido forte HCl

$$(c_H \ll c_S, c_A)$$



$$\frac{c_S}{c_S - c_H} \quad \frac{c_H}{c_A + c_H}$$

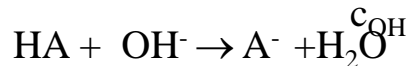
$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} = \frac{(c_S - c_H)[\text{H}_3\text{O}^+]}{(c_A + c_H)}$$

$$\simeq \text{pK}_a + \log \frac{c_S}{c_A}$$

$$[\text{H}_3\text{O}^+] = K_a \times \frac{(c_A + c_H)}{(c_S - c_H)}$$

$$\text{pH} = \text{pK}_a + \log \frac{c_S - c_H}{c_A + c_H} \simeq \text{pK}_a + \log \frac{c_S}{c_A}$$

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



$$\frac{c_A}{c_A - c_{OH}} \quad \frac{c_{OH}}{c_S + c_{OH}}$$

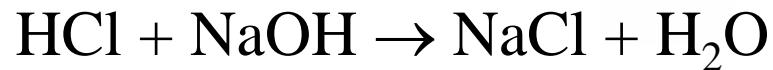
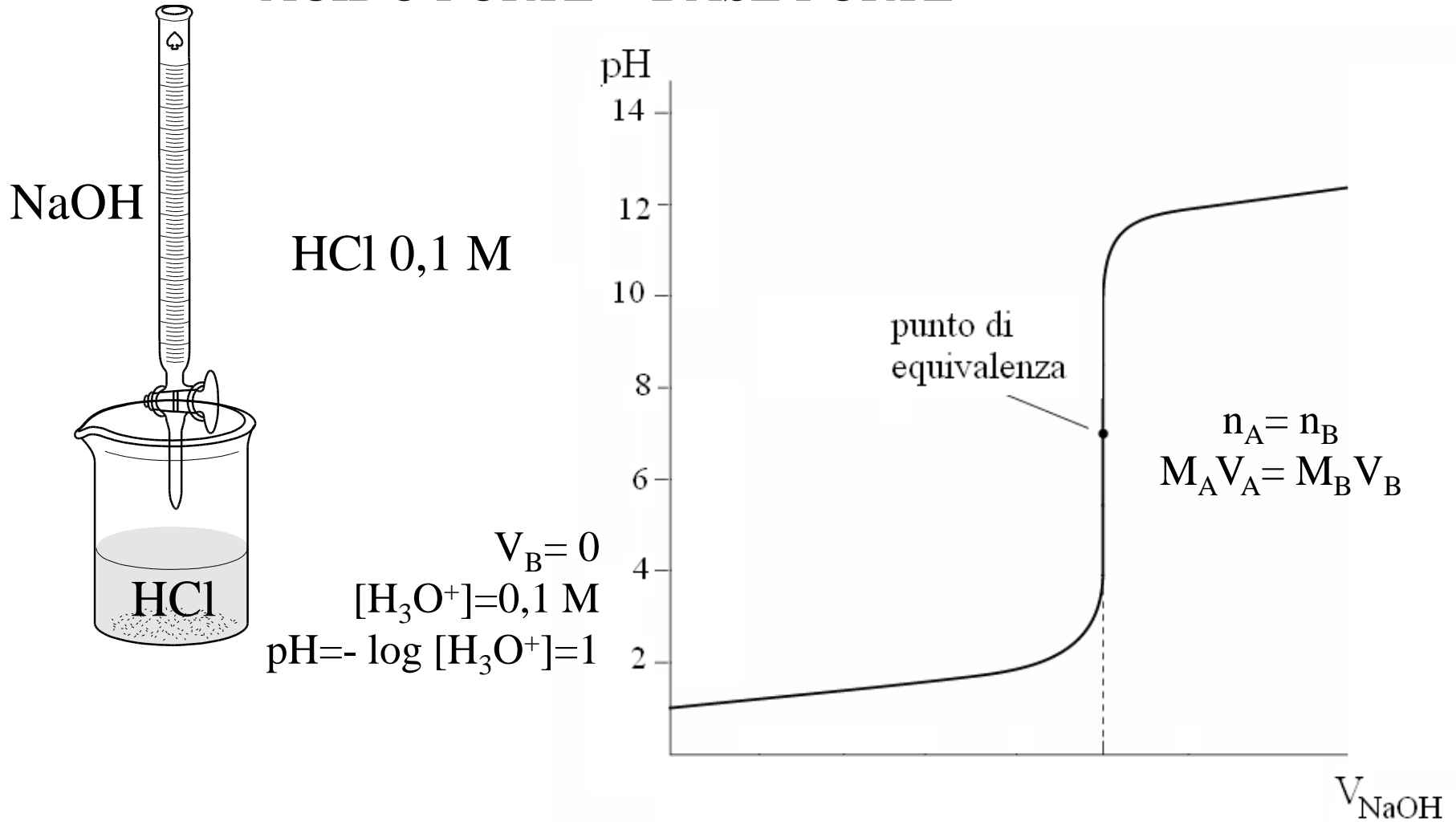
$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} = \frac{(c_S + c_{OH})[\text{H}_3\text{O}^+]}{(c_A - c_{OH})}$$

$$[\text{H}_3\text{O}^+] = K_a \frac{(c_A - c_{OH})}{(c_S + c_{OH})}$$

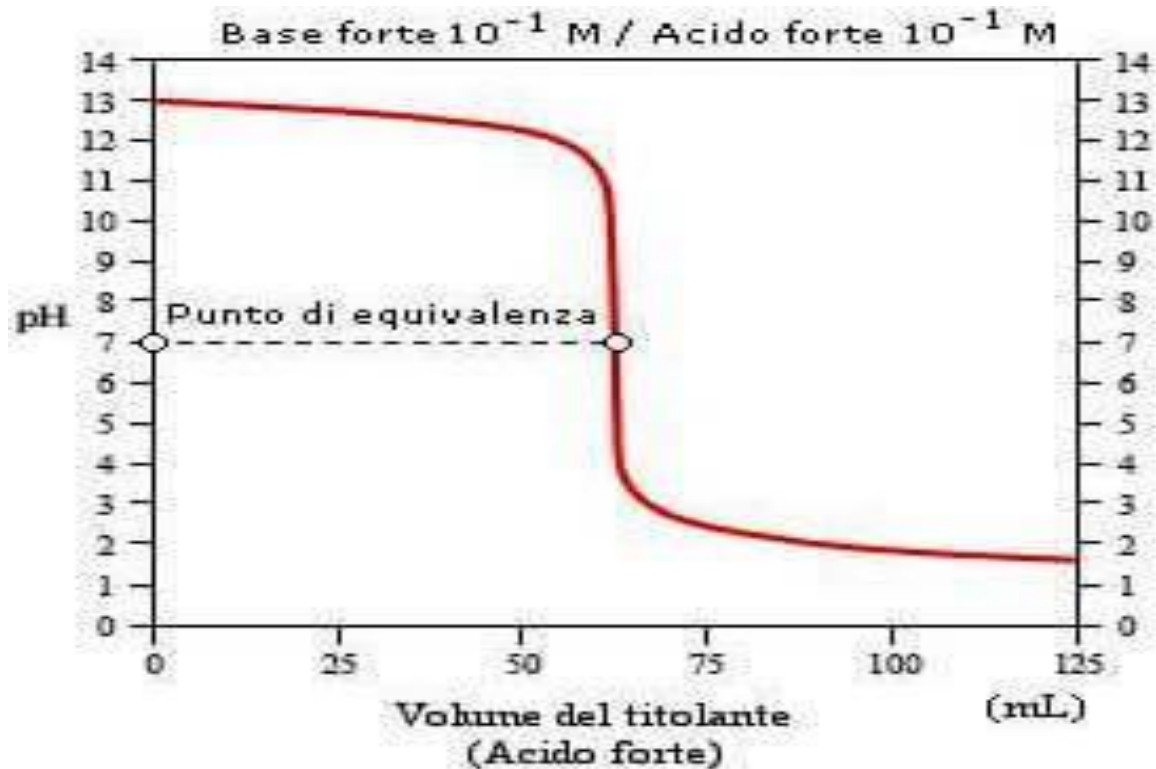
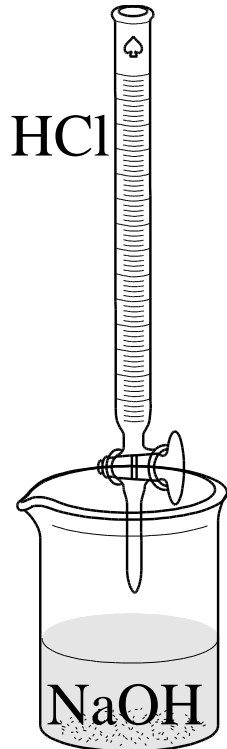
$$\text{pH} = \text{pK}_a + \log \frac{c_S + c_{OH}}{c_A - c_{OH}}$$

TITOLAZIONI ACIDO-BASE

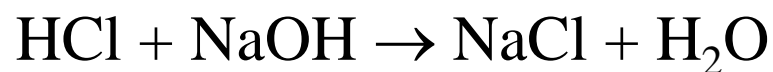
ACIDO FORTE - BASE FORTE



BASE FORTE - ACIDO FORTE

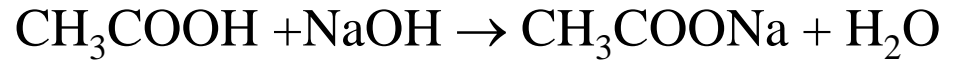


$$V_A = 0 \quad [\text{OH}^-] = 0,1 \text{ M} \quad \text{pOH} = -\log [\text{OH}^-] = 1 \quad \text{pH} = 14 - \text{pOH} = 13$$

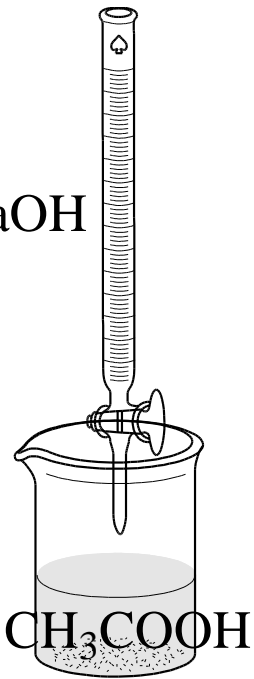


$$N_A V_A = N_B V_B$$

ACIDO DEBOLE - BASE FORTE



NaOH



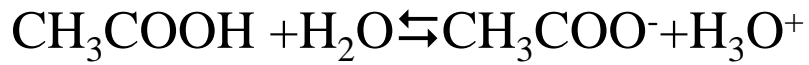
CH₃COOH

0,10 M = c

K_a = 1,8 × 10⁻⁵

NaOH 0,1 M

CH₃COOH



c - x ~ c

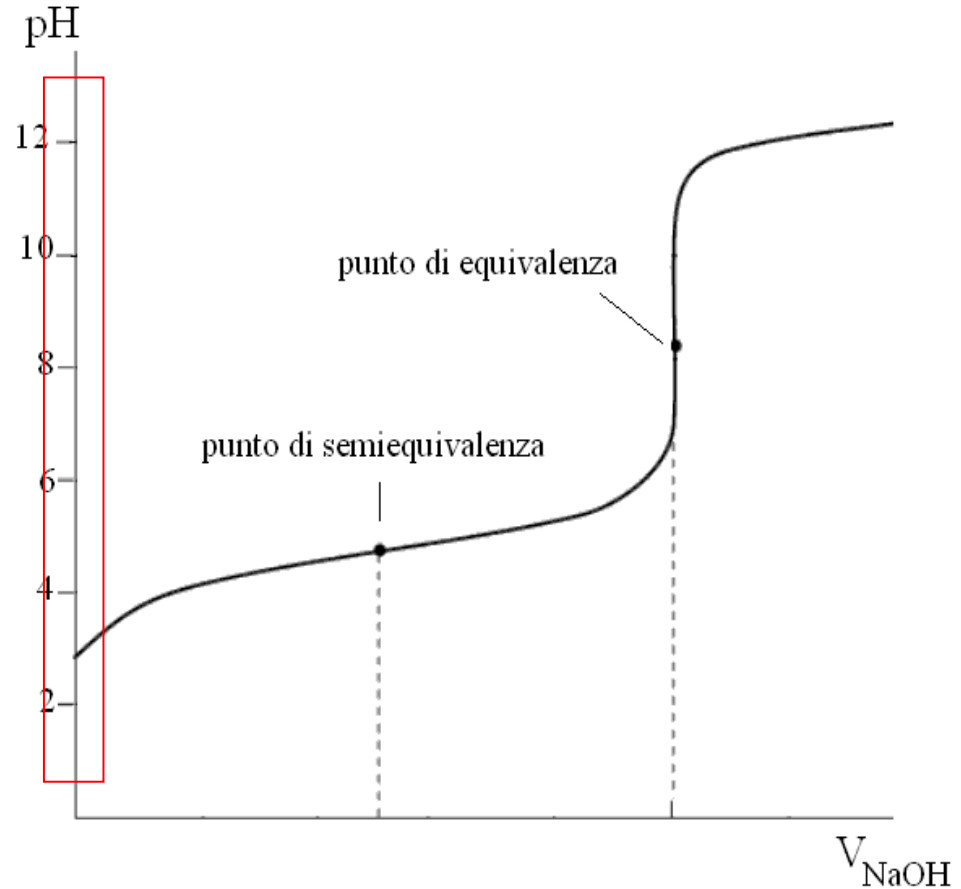
x

x

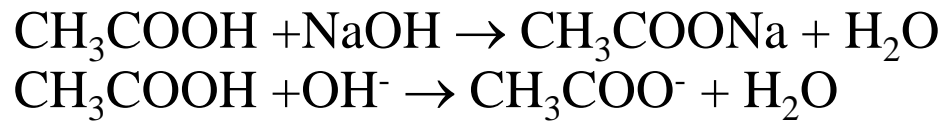
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{c}$$

$$[\text{H}_3\text{O}^+] = x = \sqrt{K_a \times c} = \sqrt{1,8 \times 10^{-5} \times 0,1} = 1,34 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2,9$$



$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times c} = \sqrt{1,8 \times 10^{-5} \times 0,1} = 1,34 \times 10^{-3} \text{ M}$$
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 2,9$$

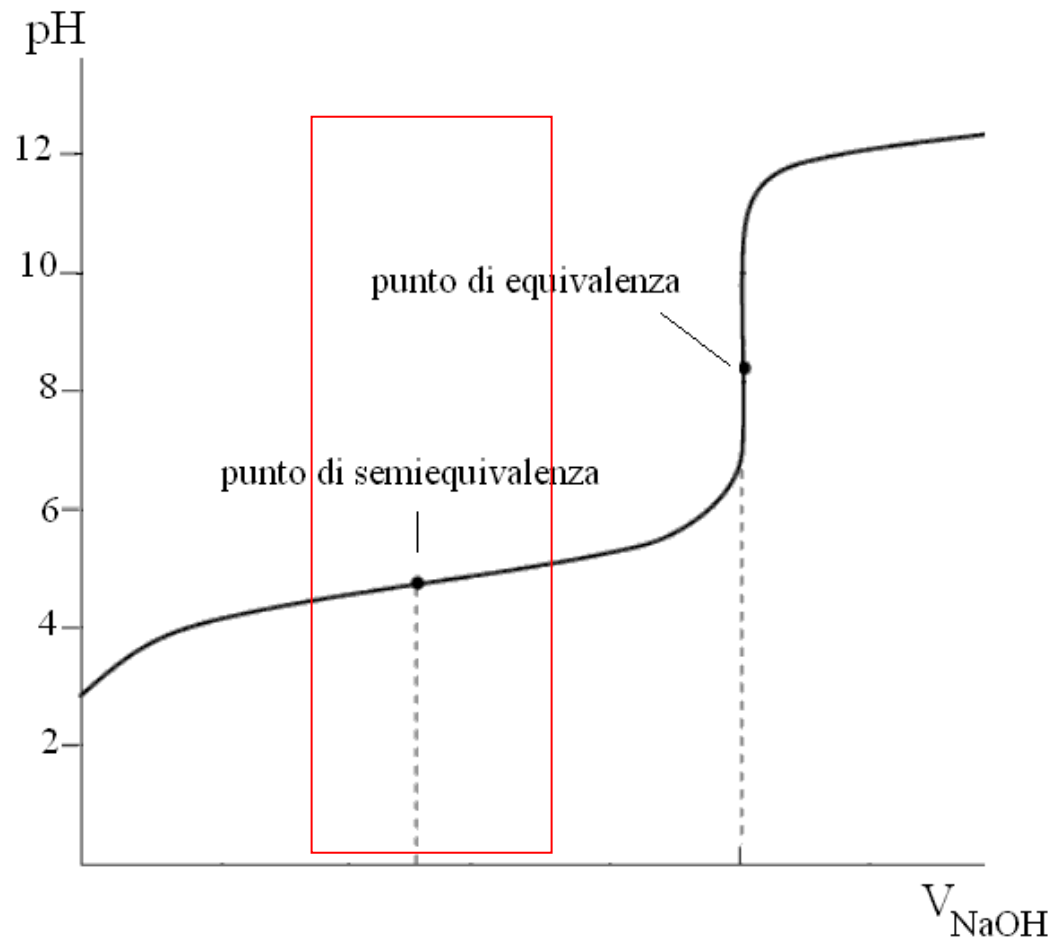


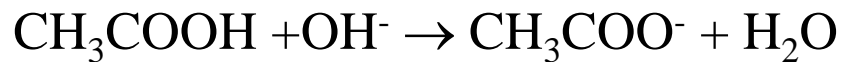
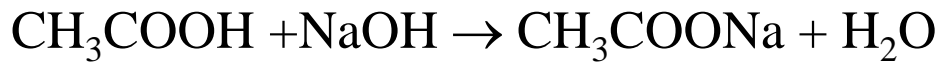
➡ Si forma una soluzione tampone

$$\text{pH} = \text{pK}_a + \log \frac{c_S}{c_A}$$

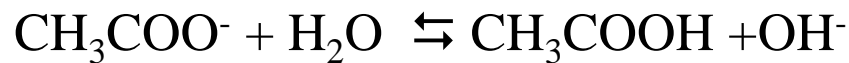
50% di titolante aggiunto

$$c_A = c_S \quad \text{pH} = \text{pK}_a$$



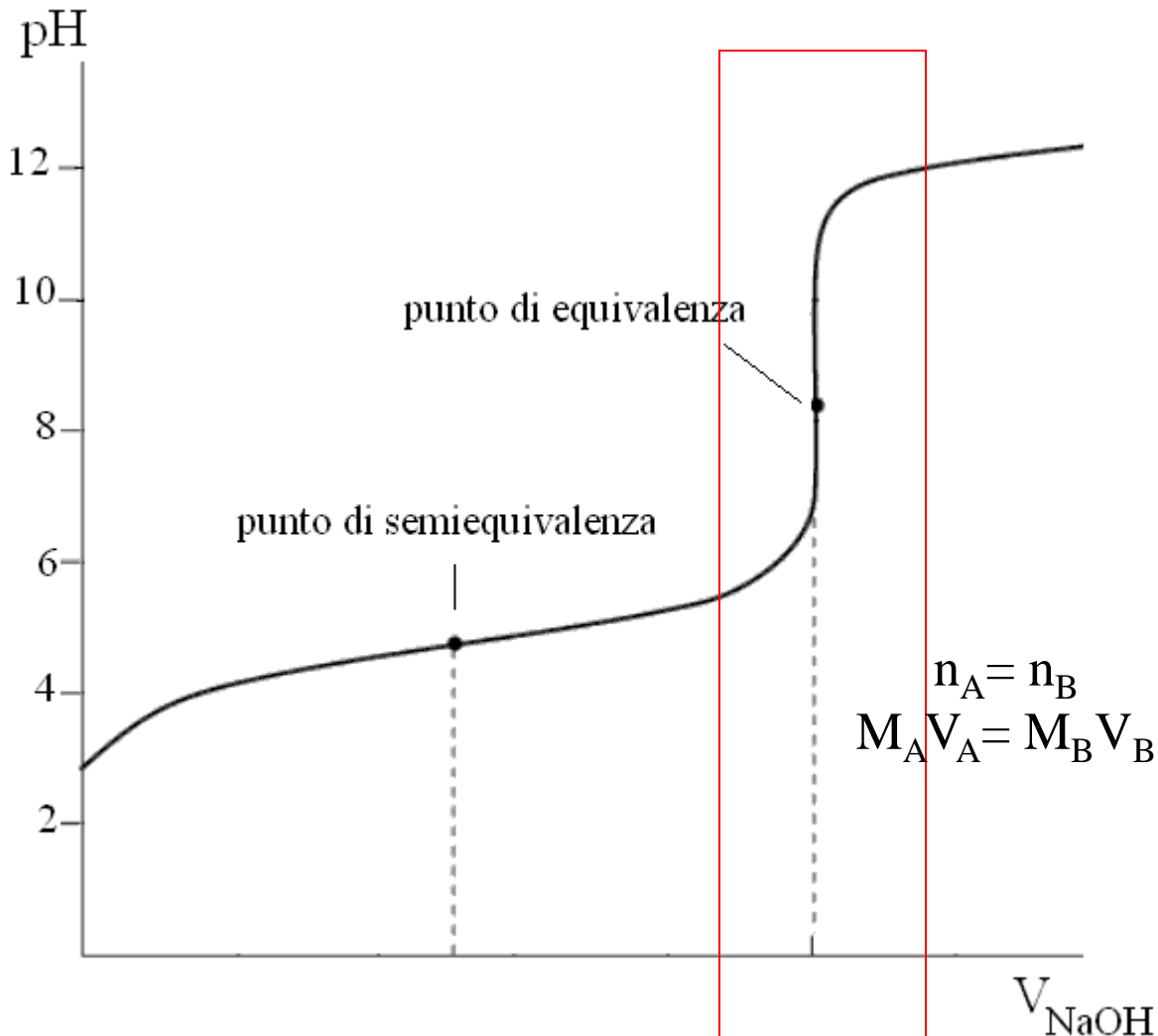


Punto di equivalenza



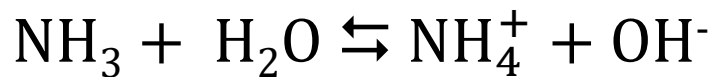
$$K_i = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

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



Base debole/acido forte: NH_3/HCl

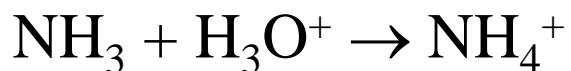
Situazione iniziale



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1,8 \times 10^{-5}$$

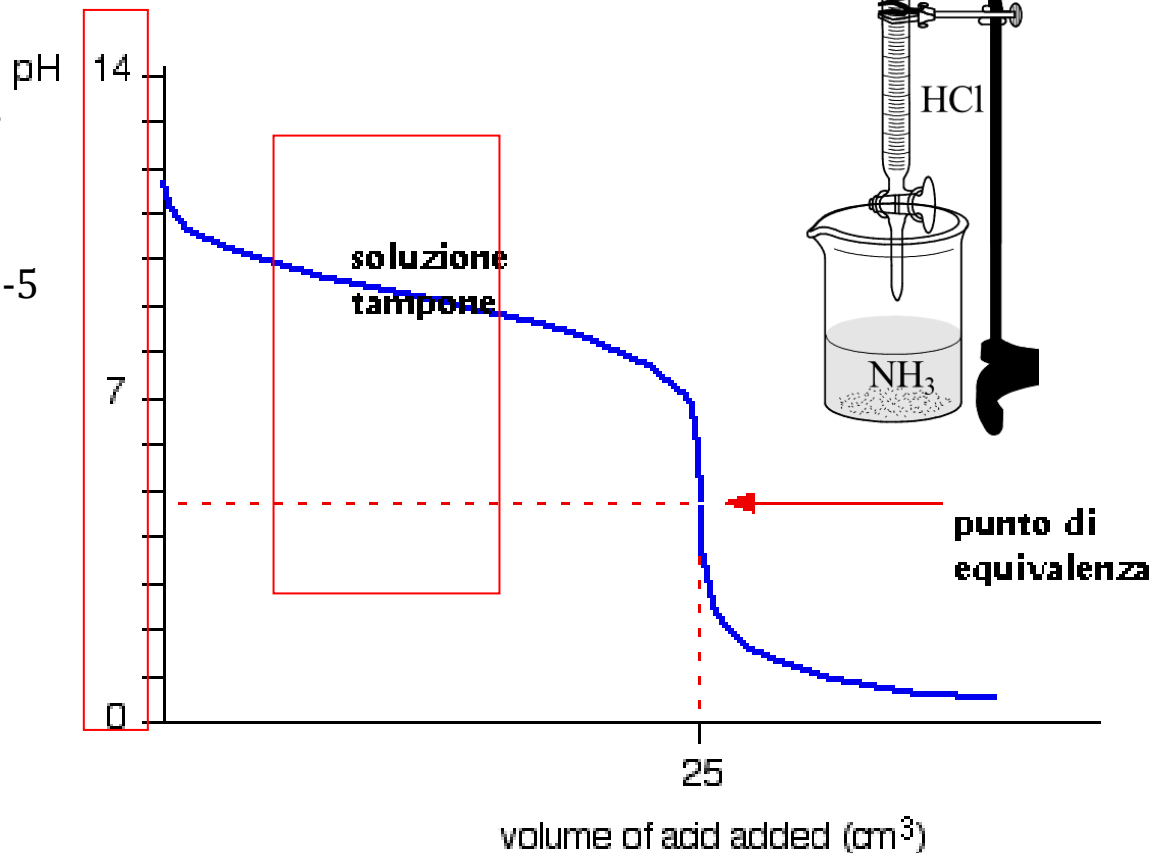
$$[\text{OH}^-] = \sqrt{K_b \times c}$$

Reazione:



Soluzione tampone

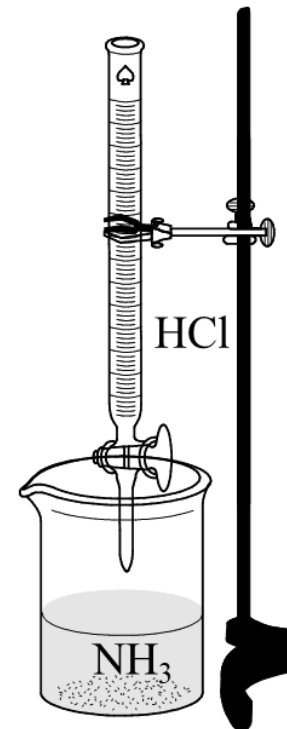
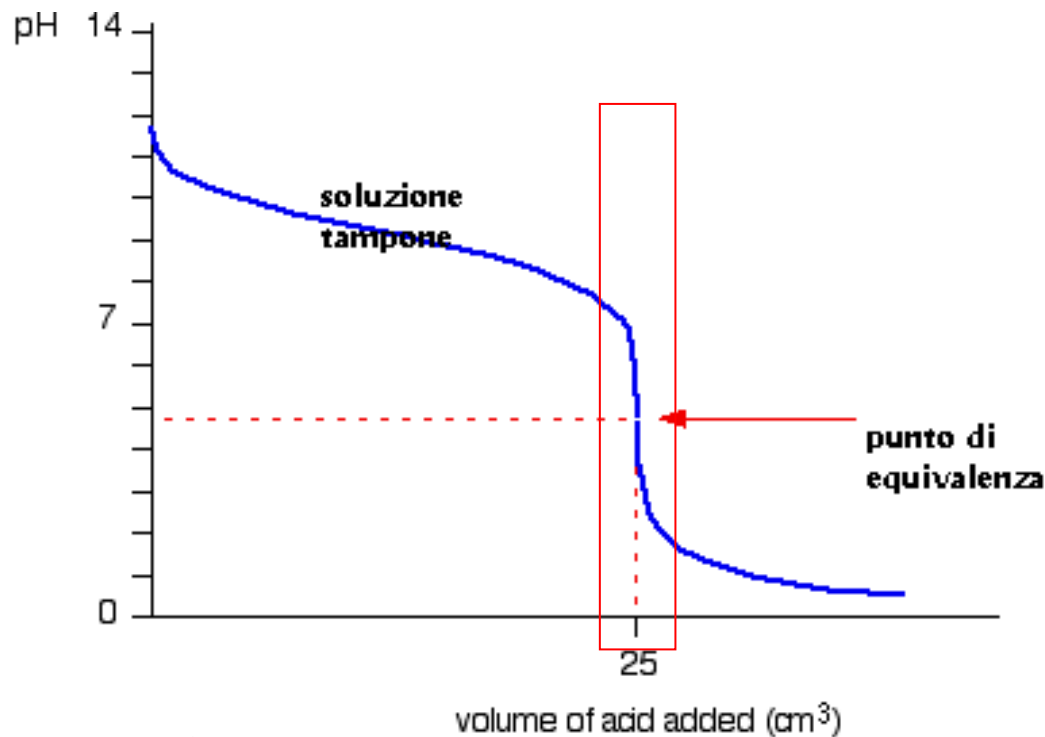
$$\begin{aligned} \text{pOH} &= -\log [\text{OH}^-] = \text{p}K_b + \log \frac{c_S}{c_B} \\ \text{pOH} &= 14 - \text{pH} \end{aligned}$$



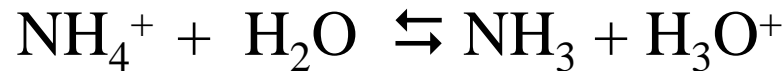
semiequivalenza $c_S = c_B$

$$\text{pOH} = \text{p}K_b = 4,75$$

$$\text{pH} = 14 - \text{pOH} = 9,25$$



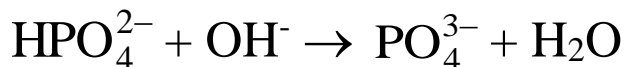
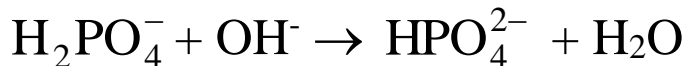
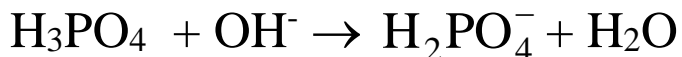
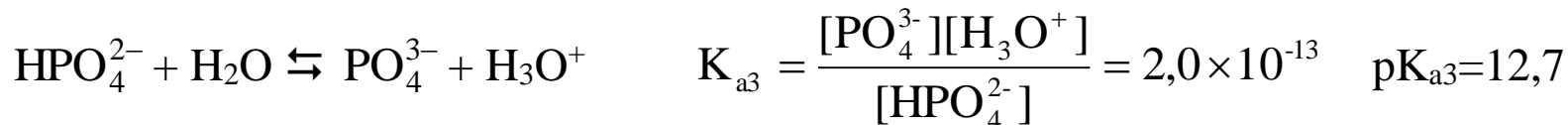
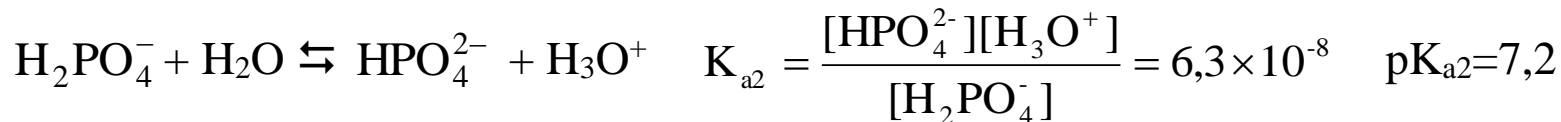
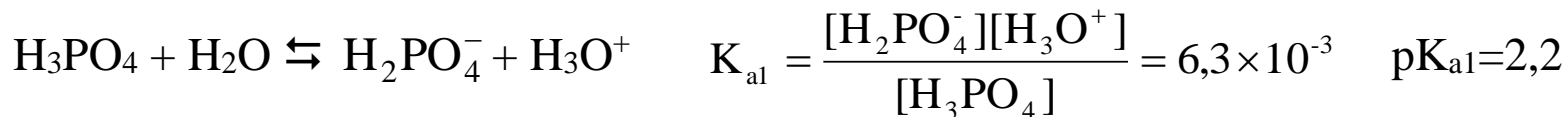
All'equivalenza:



$$K_i = K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{K_W}{K_b}$$

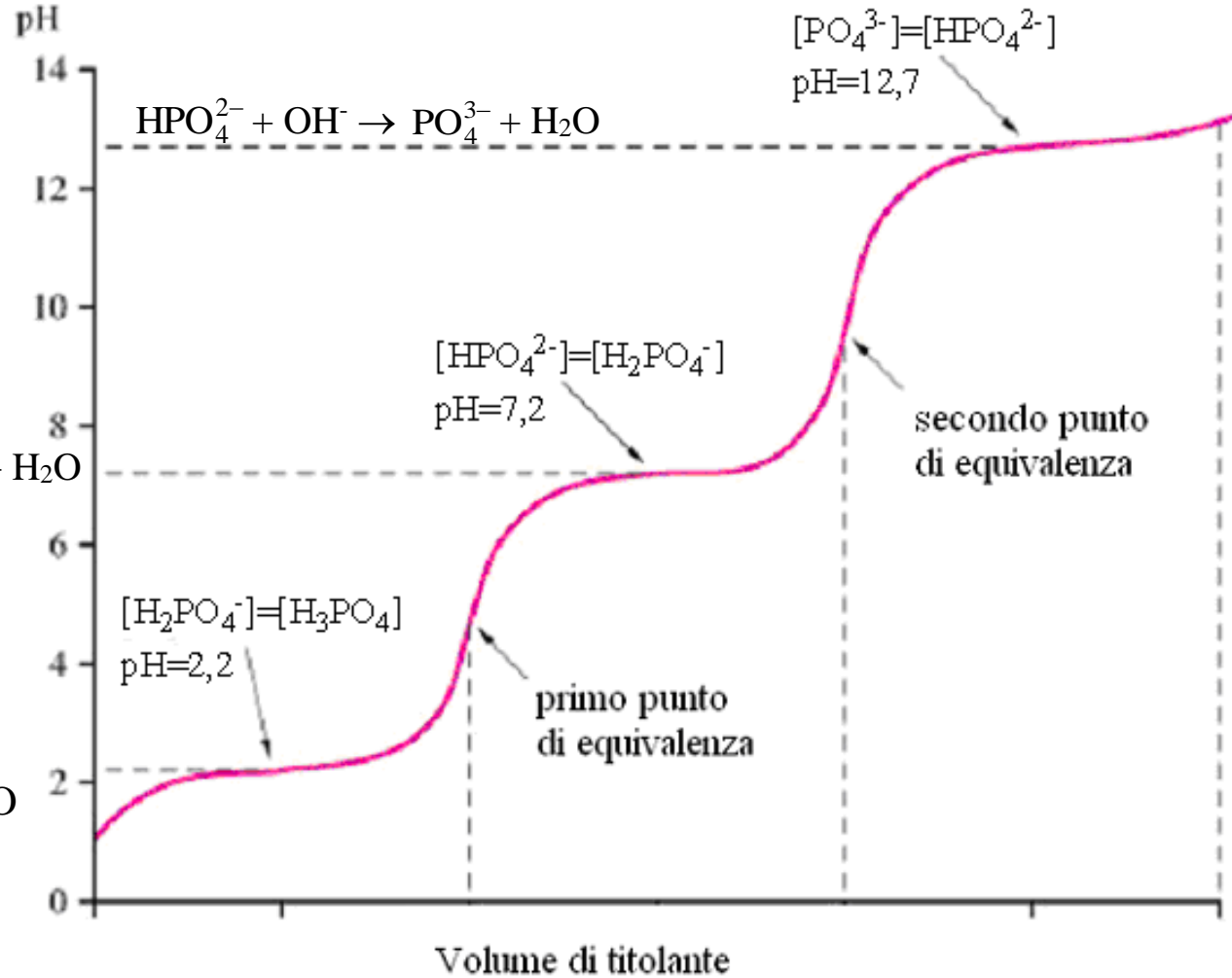
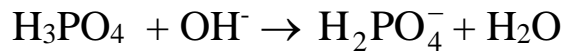
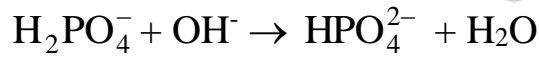
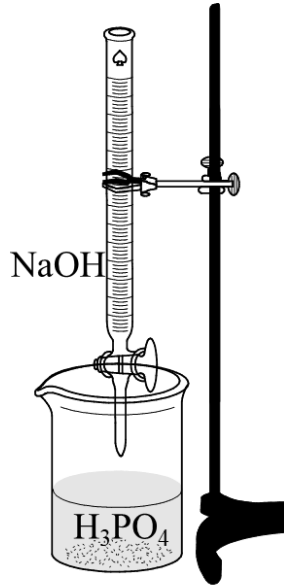
pH acido

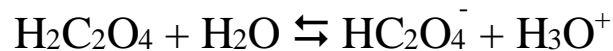
TITOLAZIONI ACIDI POLIPROTICI



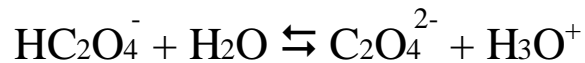
$$K_{a1}/K_{a2} \geq 10^4 \quad K_{a2}/K_{a3} \geq 10^4 \quad \Delta\text{p}K_a \geq 4$$

Titolazione $\text{H}_3\text{PO}_4/\text{NaOH}$

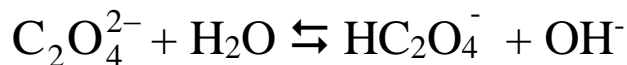
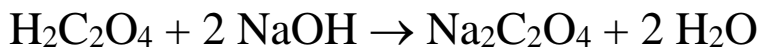
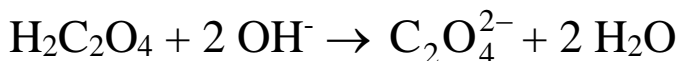
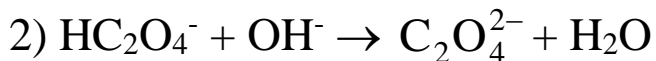
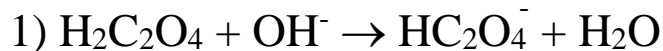




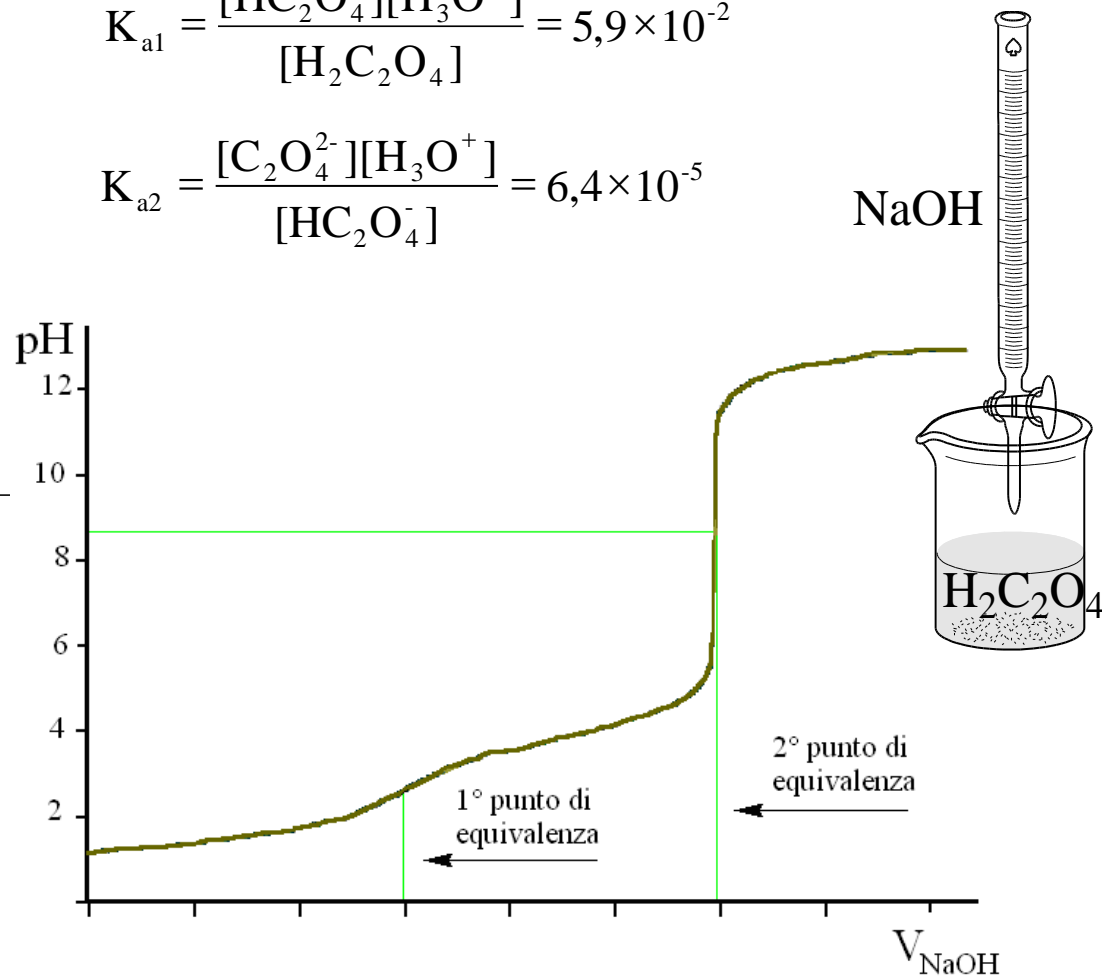
$$K_{a1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} = 5,9 \times 10^{-2}$$



$$K_{a2} = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{O}_4^-]} = 6,4 \times 10^{-5}$$



$$K_i = \frac{[\text{HC}_2\text{O}_4^-][\text{OH}^-]}{[\text{C}_2\text{O}_4^{2-}]} = \frac{K_W}{K_{a2}} = \frac{10^{-14}}{5,2 \times 10^{-5}} = 1,9 \times 10^{-10}$$

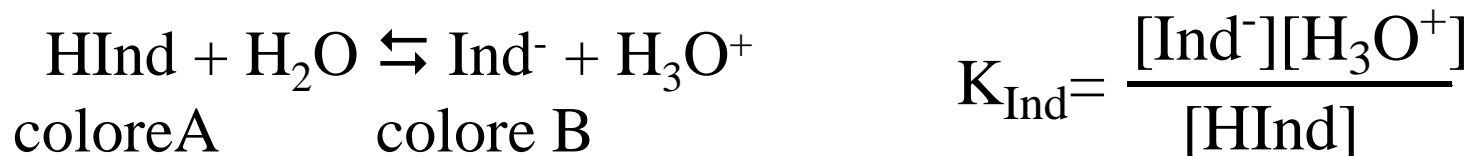


Punto finale di una titolazione:

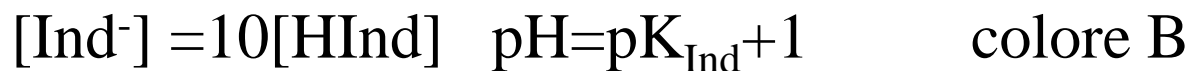
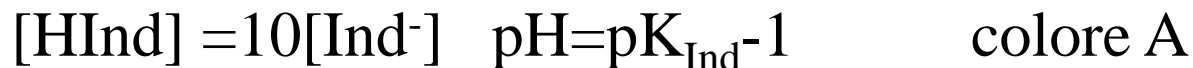
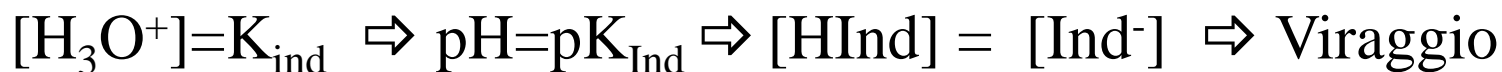
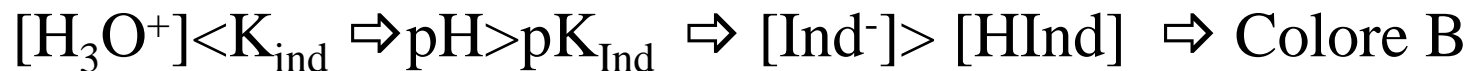
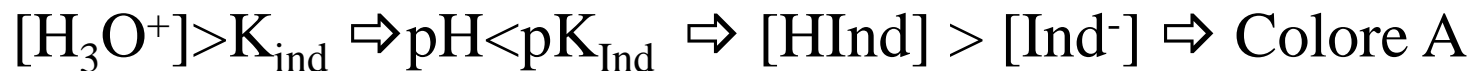
a) Metodi strumentali

b) Indicatori

Indicatori acido-base



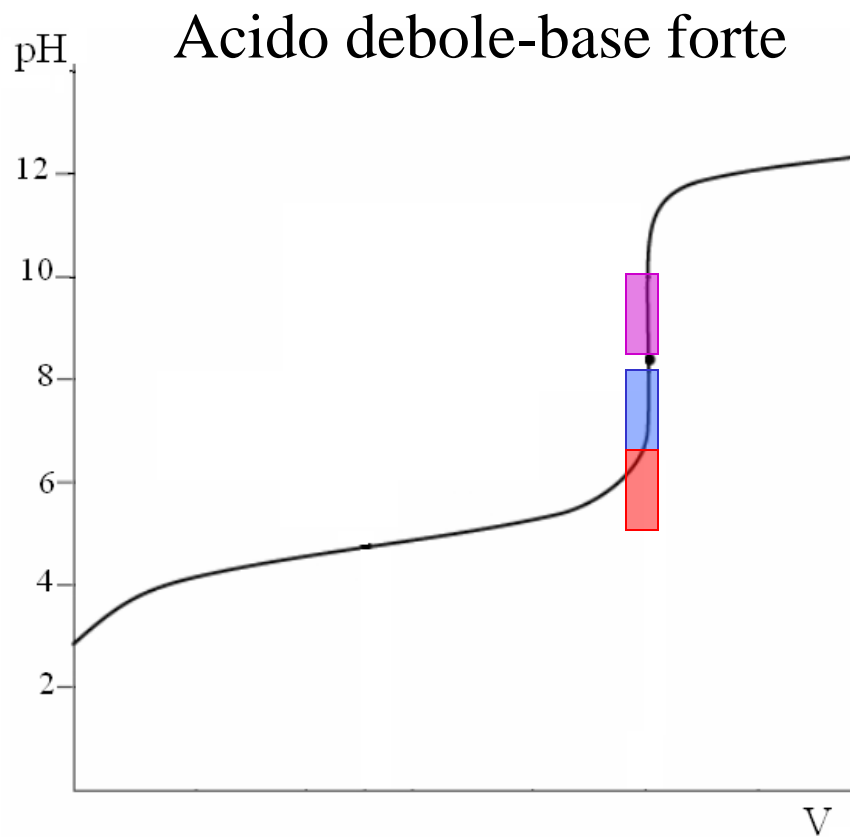
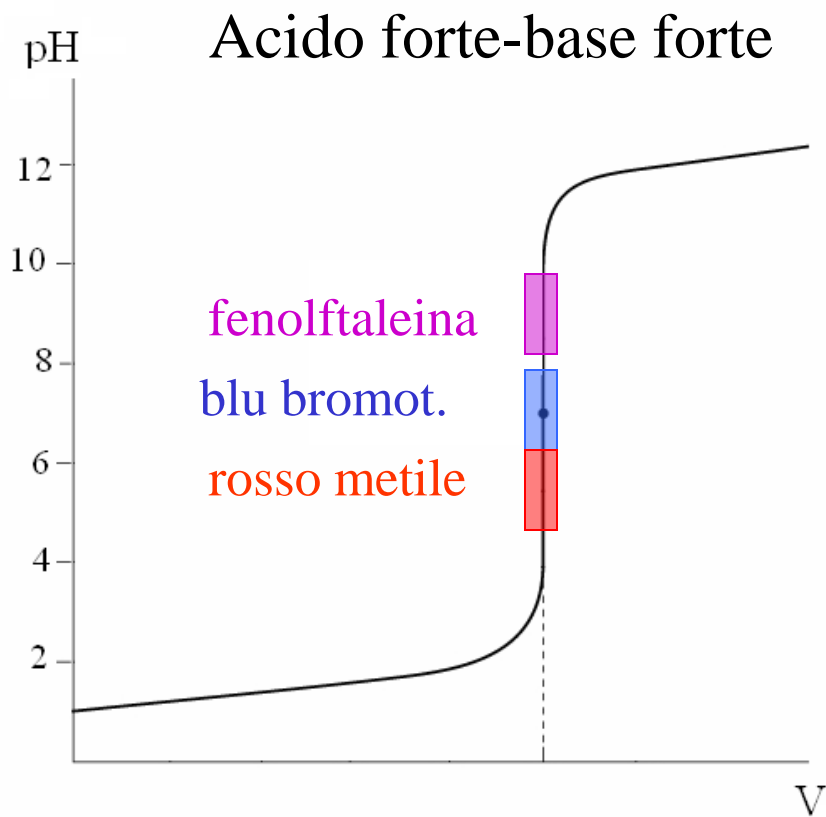
$$[\text{H}_3\text{O}^+] = K_{\text{Ind}} \frac{[\text{HInd}]}{[\text{Ind}^-]} \implies \text{pH} = \text{p}K_{\text{Ind}} + \log \frac{[\text{Ind}^-]}{[\text{HInd}]}$$



$\text{pH} = \text{p}K_{\text{Ind}} \pm 1$ intervallo di viraggio

Indicatore	pK_{Ind}	Intervallo
metilarancio	3,7	3,1 – 4,4
rosso metile	5,1	4,4 – 6,2
blu bromotimolo	7,0	6,2 – 7,6
rosso fenolo	7,9	6,4 – 8,0
fenolftaleina	9,4	8,0 – 10,0

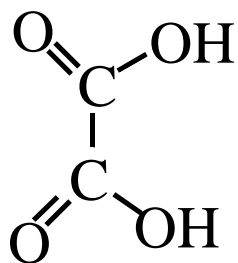
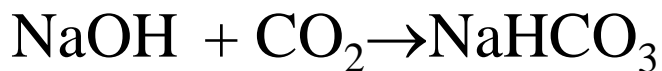
col. A	col. B
rosso	giallo
rosso	giallo
giallo	blu
giallo	rosso
incolore	viola



Esperienza 1 – Titolazione $\text{H}_2\text{C}_2\text{O}_4/\text{NaOH}$

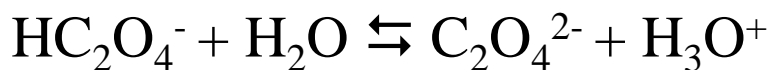
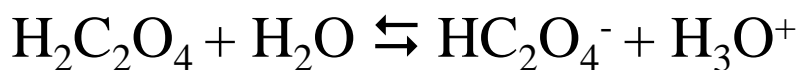
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ sostanza madre

NaOH assorbe H_2O , CO_2



$$K_{a1} = 5,9 \cdot 10^{-2}$$

$$K_{a2} = 6,4 \cdot 10^{-5}$$



$$K_{a1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

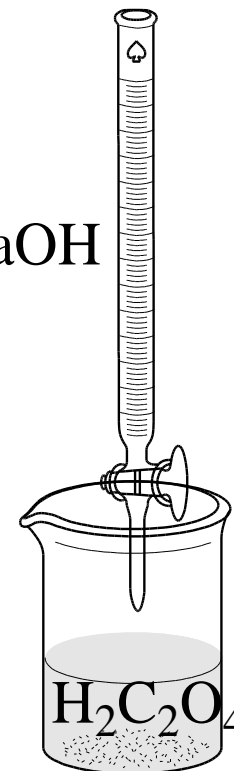
$$K_{a2} = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{O}_4^-]}$$

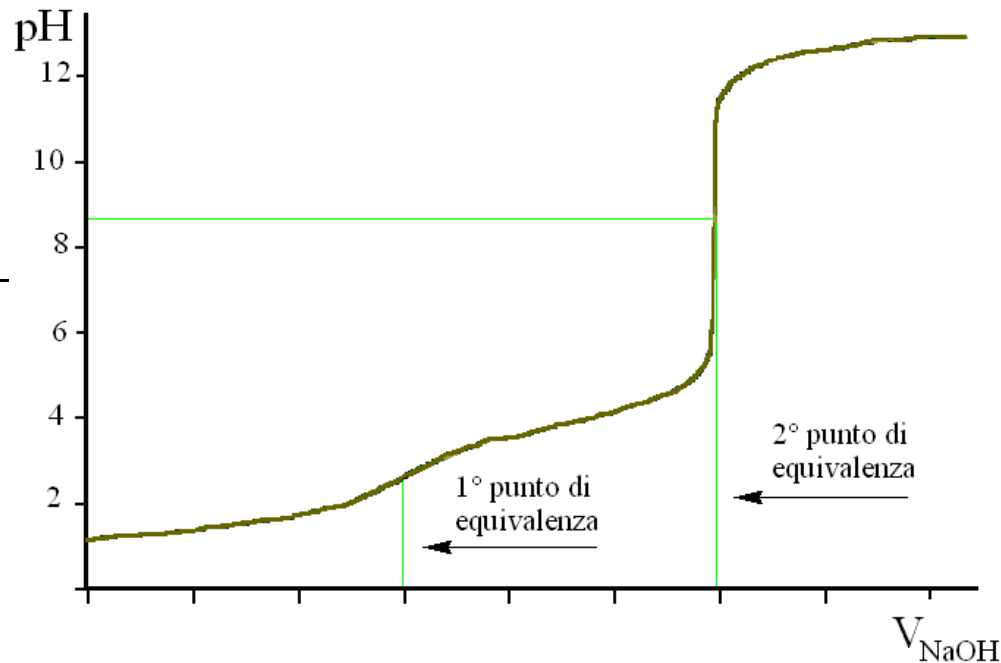
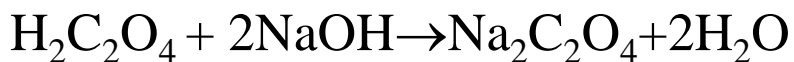
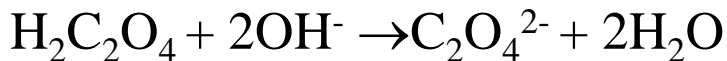
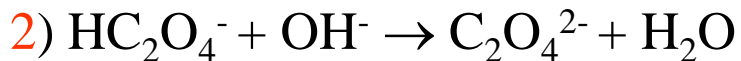
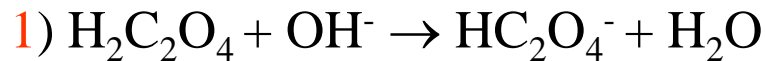


$$g_{\text{NaOH}} = N_B V_B \text{P}_{\text{eq}_{\text{NaOH}}}$$

$$g_{\text{H}_2\text{C}_2\text{O}_4} = N_a V_B \text{P}_{\text{eq}_{\text{H}_2\text{C}_2\text{O}_4}}$$

NaOH





$$K_i = \frac{K_w}{K_{a2}} = \frac{10^{-14}}{5,2 \times 10^{-5}} = 1,9 \times 10^{-11}$$

$$K_i = \frac{[\text{HC}_2\text{O}_4^-][\text{OH}^-]}{[\text{C}_2\text{O}_4^{2-}]} = \frac{x^2}{c_S}$$

$$[\text{OH}^-] = \sqrt{K_i \cdot c_S}$$

all'equivalenza $\text{pH} \approx 9$
 \Rightarrow indicatore fenolftaleina
 $\text{pK}_a = 9,4$ Viraggio 8,2-10