ELETTROCHIMICA

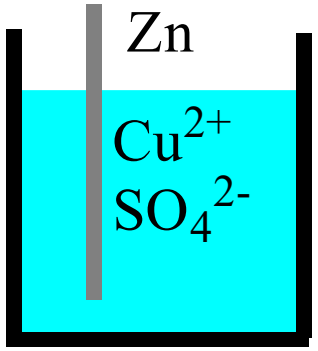
PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA per produrre LAVORO ELETTRICO

Energia chimica → Energia elettrica

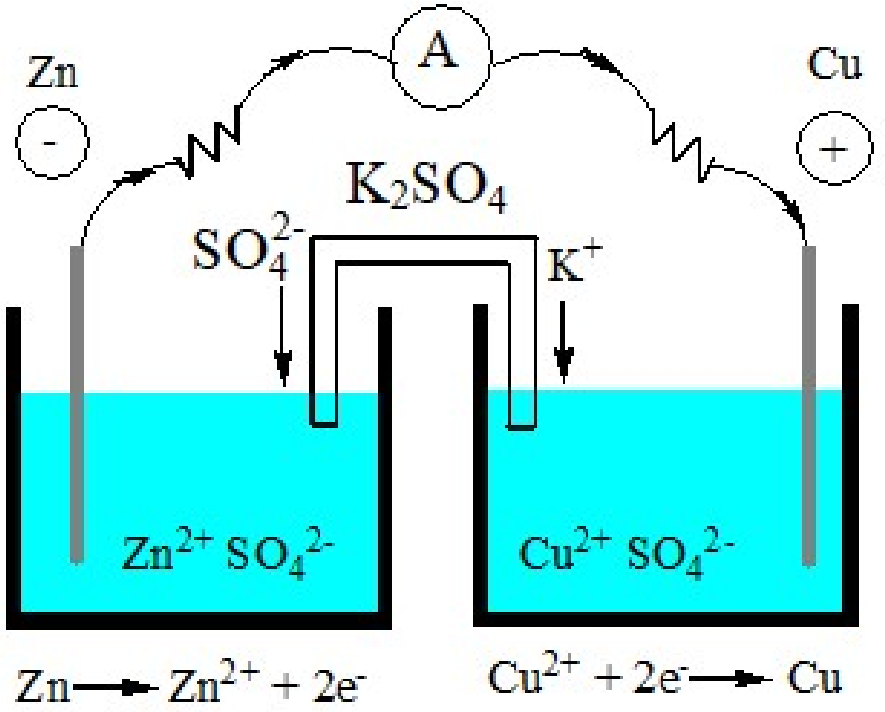
$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$

red $Cu^{2+} + 2\ e^- \rightarrow Cu^0$

ox $Zn^0 \rightarrow Zn^{2+} + 2\ e^-$



$E_{PILA} = E_+ - E_- > 0$



$Zn_{(s)} \mid Zn^{2+}_{(aq)} \mid\mid Cu^{2+}_{(aq)} \mid Cu_{(s)}$

$E_{PILA} = E_{+} - E_{-}$

E_{+} , E_{-} dipendono :
- dalla concentrazione delle specie ossidate e ridotte
- dalla loro natura chimica

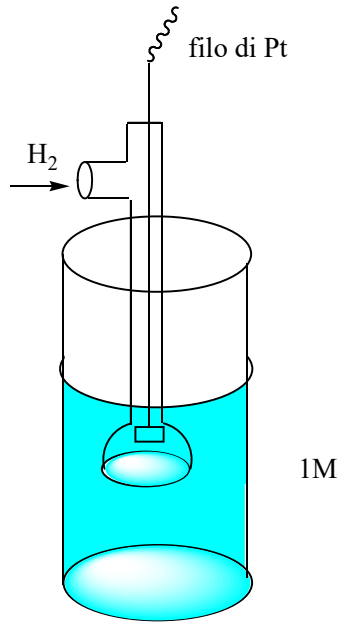
POTENZIALE STANDARD di un semielemento
→ Tutte le specie hanno concentrazione 1 molare
→ Pressione pari ad 1 atmosfera
→ T=25 °C= 298 K E°

Si può misurare la f.e.m. di una pila
non il potenziale dei singoli semielementi

Elettrodo standard a idrogeno

$2\ H^{+} + 2\ e^{-} \rightarrow H_{2\ (g)}$

$2\ H_3O^{+} + 2\ e^{-} \rightarrow H_{2\ (g)} + 2\ H_2O$



$Pt\ (H_{2(g)}, 1atm) \mid H^{+}\ (1M)$
$[H^{+}] = [H_3O^{+}] = 1\ M$

$P_{H_2} = 1\ atm$ $E°_{H^{+}/H_2} = 0$

specie ossidata	*specie ridotta*	E^0 *(V)*	
	$F_{2\ (g)} + 2e^- \leftrightarrows 2F^-_{(aq)}$		+2.87
$H_2O_{2\ (aq)} + 2H^+_{(aq)} + 2e^-$	$\leftrightarrows 2H_2O_{(l)}$	+1.77	
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^-$	$\leftrightarrows Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51	
$Au^{3+}_{(aq)} + 3e^-$	$\leftrightarrows Au_{(s)}$	+1.50	
$Cl_{2\ (g)} + 2e$	$\leftrightarrows 2Cl^-_{(aq)}$	+1.36	
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^-$	$\leftrightarrows 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33	
$O_{2\ (g)} + 4H^+_{(aq)} + 4e^-$	$\leftrightarrows 2H_2O_{(l)}$		+1.23
$ClO_4^-{}_{(aq)} + 2H^+_{(aq)} + 2e^-$	$\leftrightarrows ClO_3^-{}_{(aq)} + H_2O_{(l)}$	+1.23	
$Pt^{2+}_{(aq)} + 2e^-$	$\leftrightarrows Pt_{(s)}$	+1.20	
$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^-$	$\leftrightarrows NO_{(g)} + H_2O_{(l)}$	+0.96	
$Ag^+_{(aq)} + e^-$	$\leftrightarrows Ag_{(s)}$	+0.80	
$Cu^{2+}_{(aq)} + 2e^-$	$\leftrightarrows Cu_{(s)}$	+0.34	
$2H^+_{(aq)} + 2e$	**$\leftrightarrows H_{2(g)}$**	**+0.00**	
$Fe^{2+}_{(aq)} + 2e^-$	$\leftrightarrows Fe_{(s)}$	-0.44	
$Cr^{3+}_{(aq)} + 3e^-$	$\leftrightarrows Cr_{(s)}$	-0.74	
$Zn^{2+}_{(aq)} + 2e^-$	$\leftrightarrows Zn_{(s)}$	-0.76	
$Al^{3+}_{(aq)} + 3e^-$	$\leftrightarrows Al_{(s)}$		-1.66
$Mg^{2+}_{(aq)} + 2e^-$	$\leftrightarrows Mg_{(s)}$	-2.36	
$Na^+_{(aq)} + e^-$	$\leftrightarrows Na_{(s)}$	-2.71	
$K^+_{(aq)} + e^-$	$\leftrightarrows K_{(s)}$		-2.93
$Li^+_{(aq)} + e^-$	$\leftrightarrows Li_{(s)}$	-3.05	

$E_{PILA} = E_+ - E_-$ E_+ , E_- dipendono :

- dalla natura chimica delle specie ossidate e ridotte → E°
- dalla loro concentrazione

ox + ne^- → red

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n}\log\frac{a_{ox}}{a_{red}}$$

Equazione di Nernst

R = 0,0821 atm·l·K^{-1}= 8,31 J ·K^{-1} T = 298 K

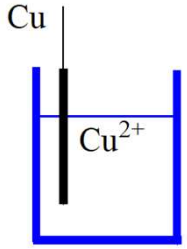
F= 96500 C Costante di Faraday

2,3 conversione da ln a log

a = attività ↗ per le specie in soluzione: concentrazione (M)
→ per i gas: pressione P
↘ per i solidi puri: 1

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n}\log\frac{a_{ox}}{a_{red}}$$

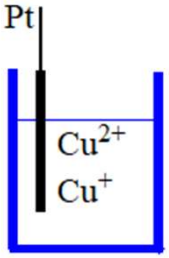
$Cu^{2+} + 2\ e^- \rightarrow Cu^0$ $\qquad E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]$



$Cu \mid Cu^{2+}$

$Cu^{2+} + e^- \rightarrow Cu^+$

$E_{Cu^{2+}/Cu^+} = E^0_{Cu^{2+}/Cu^+} + 0{,}0592\log\frac{[Cu^{2+}]}{[Cu^+]}$

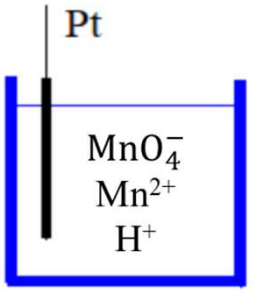


$Pt \mid Cu^{2+}, Cu^+$

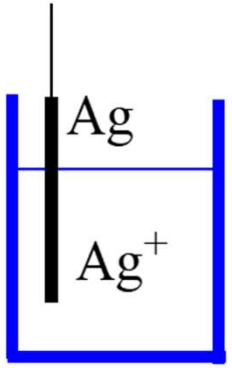
$\overset{+7}{MnO_4^-} + 5\ e^- + 8\ H^+ \rightarrow \overset{+2}{Mn^{2+}} + 4\ H_2O$

$E_{MnO_4^-/Mn^{2+}} = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}0592}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$

$Pt \mid MnO_4^-, Mn^{2+}, H^+$



Elettrodi di I specie

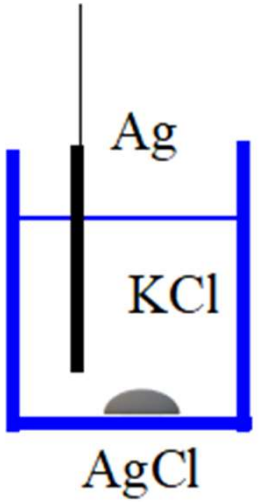


$Ag^+ + e^- \rightarrow Ag°$ $\quad Ag \mid Ag^+$

$E_{Ag^+/Ag} = E°_{Ag^+/Ag} + 0{,}059 \log[Ag^+]$

Elettrodi di II specie

$Ag \mid AgCl \mid KCl$



$Ag^+ + e^- \rightarrow Ag°$

$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ $\quad K_{PS} = [Ag^+][Cl^-] \Rightarrow [Ag^+] = K_{PS}/[Cl^-]$

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

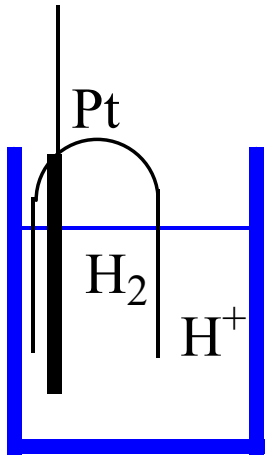
$E°_{Ag^+/Ag} + 0{,}059 \log K_{PS} - 0{,}059 \log [Cl^-] =$

$E_{AgCl/Ag} = E°_{AgCl/Ag} - 0{,}059 \log [Cl^-]$ $\quad AgCl + e^- \rightarrow Ag° + Cl^-$

Elettrodi a gas

$2H^+ + 2e^- \rightarrow H_2$ $\qquad$ $Pt, H_2 | H^+$

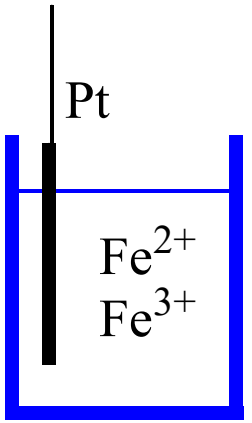
$$E_{H^+/H_2} = E^0_{H^+/H_2} + \frac{0{,}0592}{2} \log \frac{a^2_{H^+}}{a_{H_2}} = \frac{0{,}0592}{2} \log \frac{[H^+]^2}{P_{H_2}}$$



Elettrodi redox

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\qquad$ $Pt, | Fe^{2+}, Fe^{3+}$

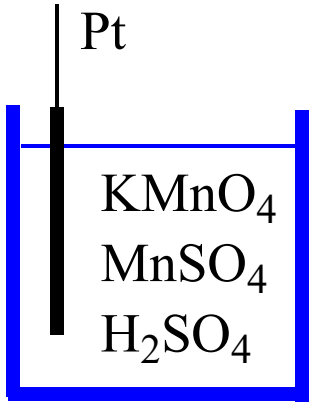
$$E_{Fe^{3+}/Fe^{2+}} = E°_{Fe^{3+}/Fe^{2+}} + 0{,}059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$



$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

$Pt \,|\, KMnO_4, MnSO_4, H_2SO_4$

$$E_{MnO_4^-/Mn^{2+}} = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}0592}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

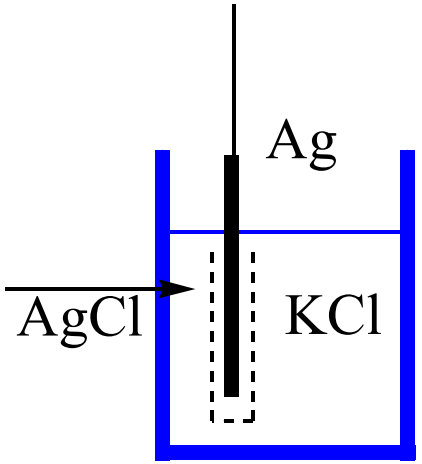


Potenziometria

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

Elettrodo di misura

Elettrodo di riferimento



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

$Ag^+ + e^- \rightarrow Ag°$

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

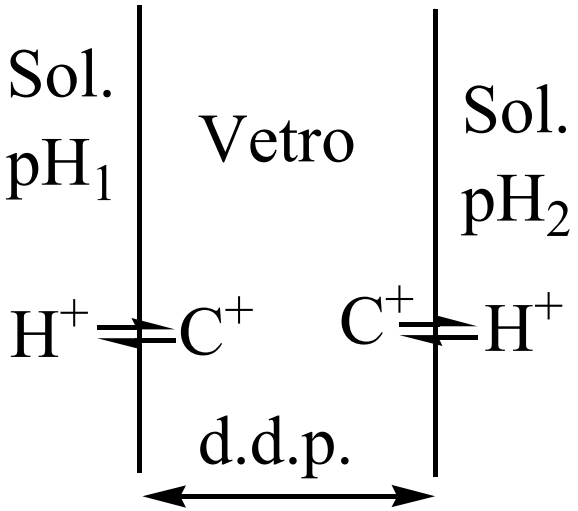
$K_{PS} = [Ag^+][Cl^-] \Rightarrow [Ag^+] = K_{PS}/[Cl^-]$

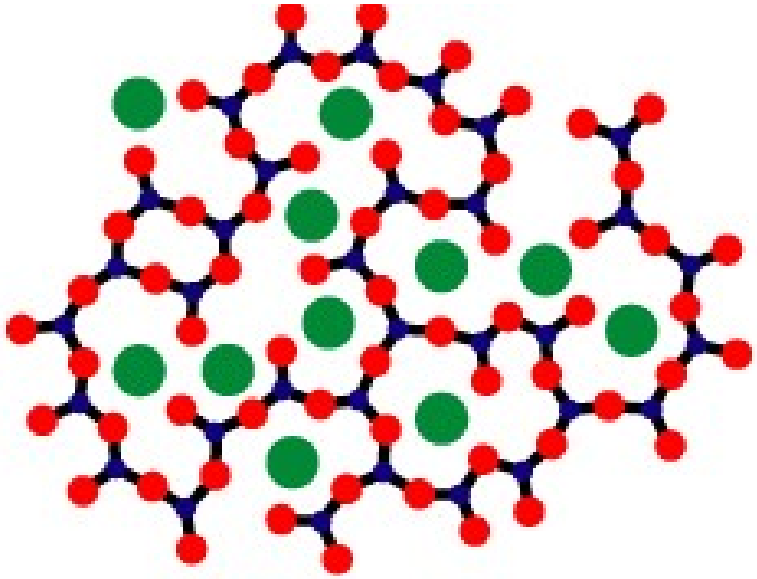
$E_{Ag^+/Ag} = E°_{Ag^+/Ag} + 0{,}059 \log [Ag^+] = E°_{Ag^+/Ag} + 0{,}059 \log(K_{PS}/[Cl^-])$

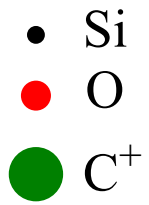
Elettrodi a membrana → scambio ionico

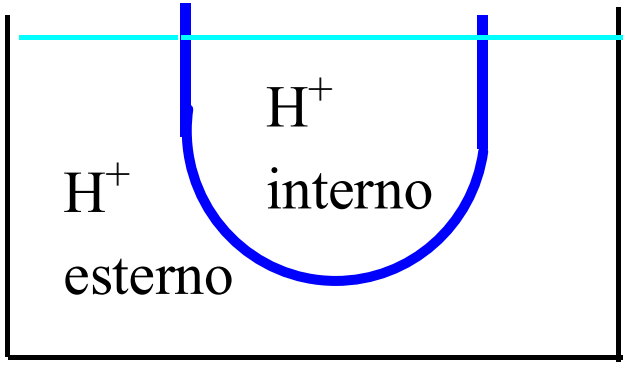
Elettrodo a vetro → H_3O^+

Vetro: tetraedri SiO_4









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

pHmetro

Elettrodo a vetro

Membrana di vetro

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

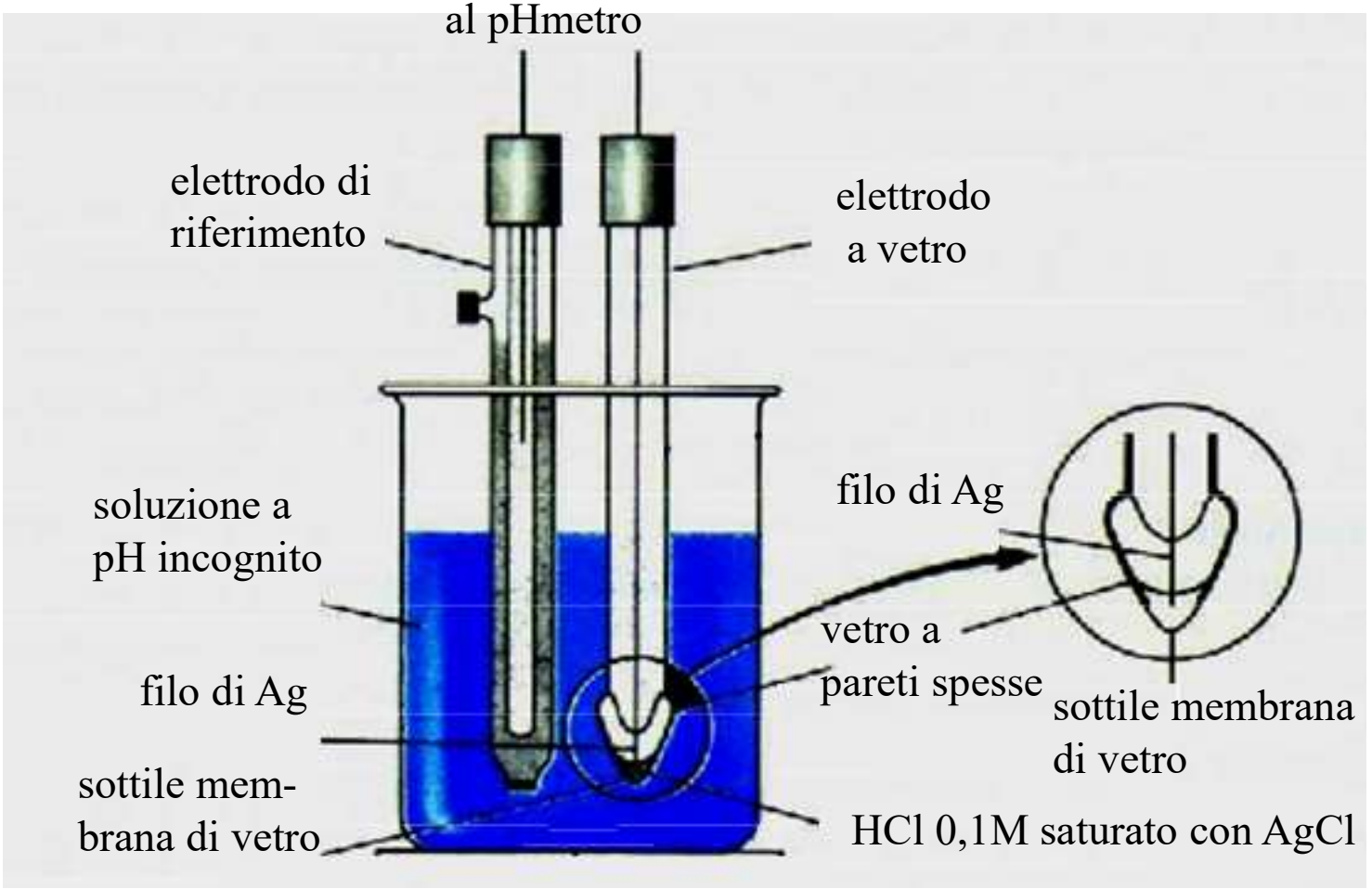
Elettrodo di riferimento

$[H^+]$ esterna (analita)

$[H^+]$ interno costante

Elettrodo di riferimento interno

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



pHmetro

F.e.m. = differenza di potenziale ai capi della pila quando non eroga corrente
Circuito potenziometrico

Elettrodi a membrana ionoselettivi (es. Na^+)

Elettrodi ionoselettivi a stato solido (es. F^-)

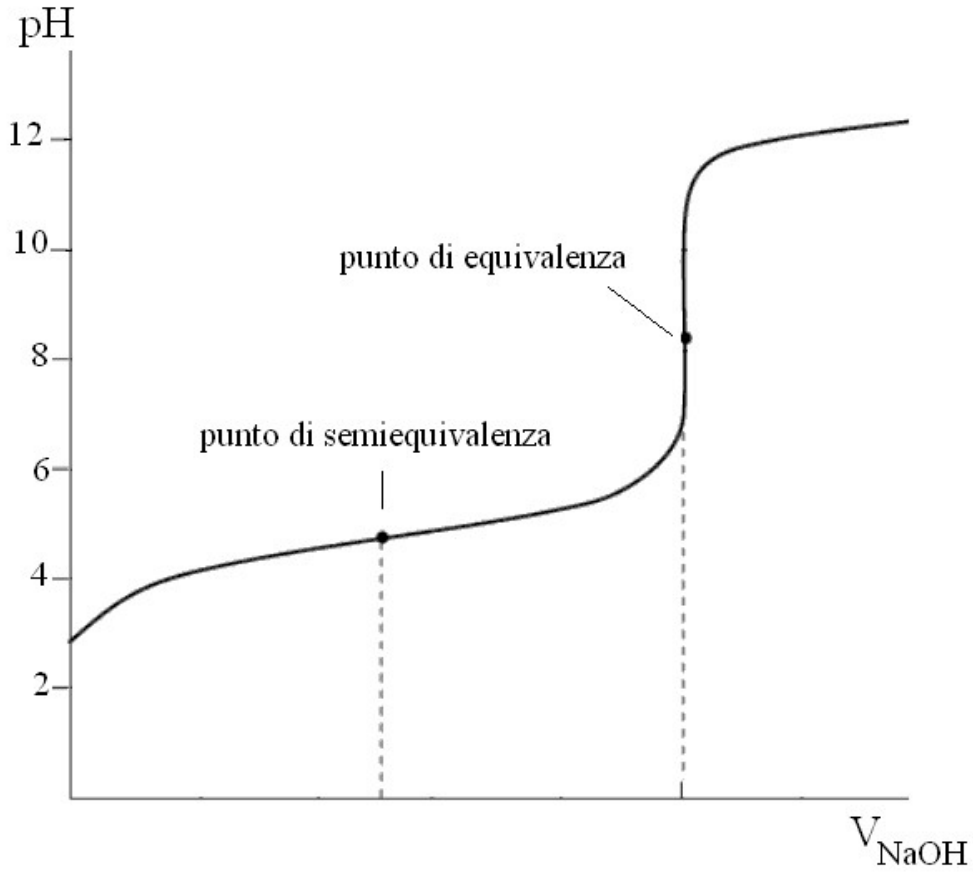
$LaF_{3(s)} \rightleftarrows La^{3+} + 3\ F^-$ $\qquad K_{PS}=[La^{3+}][F^-]^3$

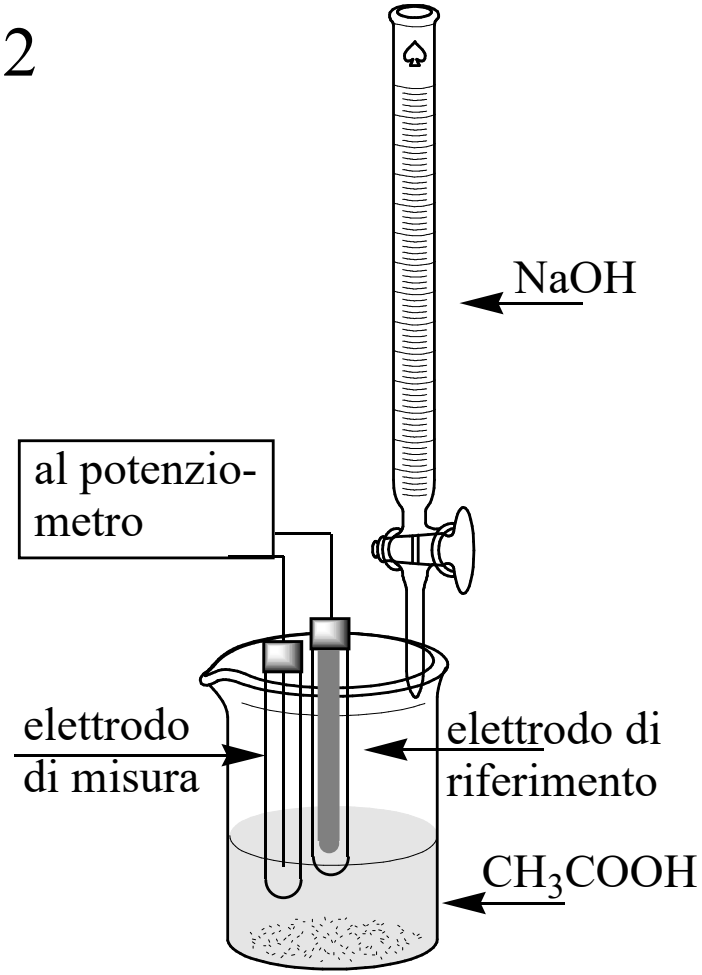
Elettrodi gas-sensibili (es. CO_2, NH_3)

$CO_2 + H_2O \leftrightarrows HCO_3^- + H^+$ $\qquad NH_3+H_2O \leftrightarrows NH_4^+ + OH^-$

Elettrodi a enzima $\qquad CO(NH_2)_2 + H_2O \xrightarrow{\text{ureasi}} 2\ NH_3 + CO_2$

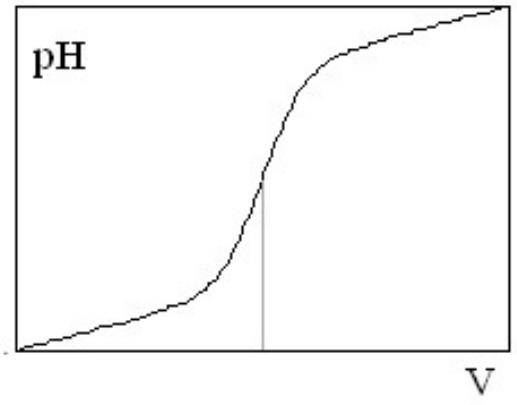
Titolazioni potenziometriche esp. 2

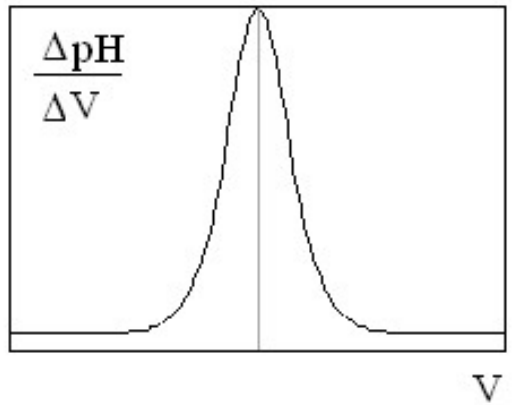




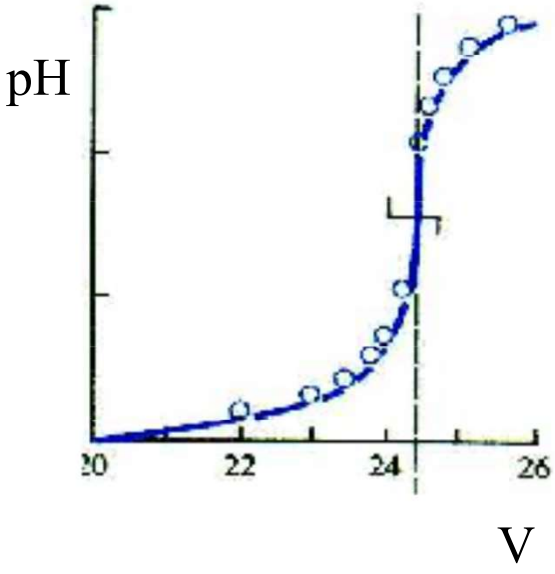
Metodo delle derivata prima

V_{NaOH}	pH	ΔpH	ΔV	$\frac{\Delta pH}{\Delta V}$

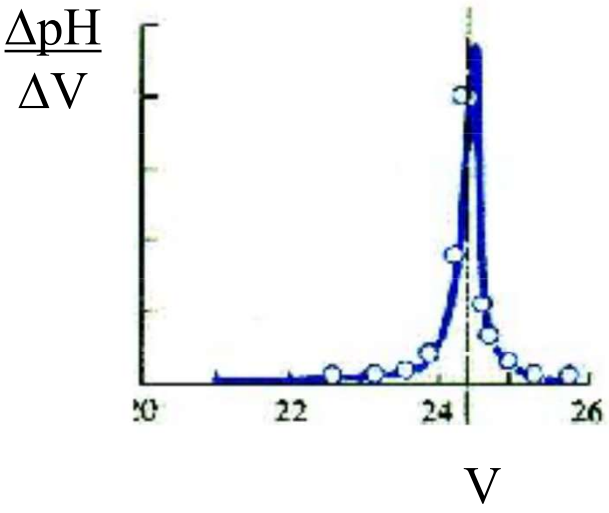




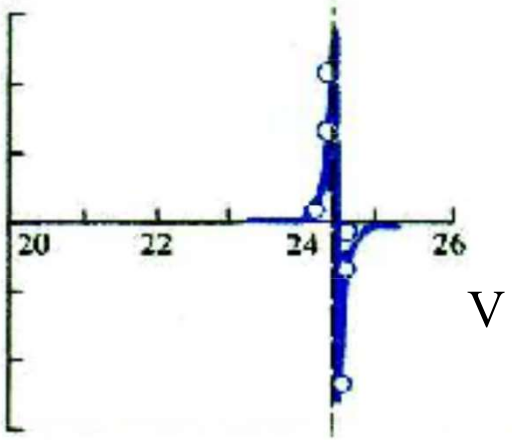
Metodo delle derivate



Derivata prima



Derivata seconda



V_{NaOH}	pH	$\frac{\Delta pH}{\Delta V}$	$\frac{\Delta^2 pH}{\Delta V^2}$

Ossidoriduzioni

H_2O

$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$

Zn

$\overset{0}{Zn} + Cu^{2+} \rightarrow Zn^{2+} + \overset{0}{Cu}$

red

ox

riducente → $Zn \rightarrow Zn^{2+} + 2\ e^-$ semireazione di ossidazione

ossidante → $Cu^{2+} + 2\ e^- \rightarrow Cu$ riduzione

$Zn + Cu^{2+} + 2\ e^- \rightarrow Cu + Zn^{2+} + 2\ e^-$

Scambio di elettroni

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

ossidoriduzion

Metodo ionico-elettronico

Reazioni in soluzione acquosa

red

$Cu^{2+} + Al \rightarrow Cu + Al^{3+}$

ox

$Al \rightarrow Al^{3+} + 3\ e^-$ | x2

$Cu^{2+} + 2\ e^- \rightarrow Cu$ | x3

$3\ Cu^{2+} + 6\ e^- + 2\ Al \rightarrow 3\ Cu + 2\ Al^{3+} + 6\ e^-$

$3\ Cu^{2+} + 2\ Al \rightarrow 3\ Cu + 2\ Al^{3+}$

red

0 +1 -1 +2 -1 0

$Zn + HCl \rightarrow ZnCl_2 \uparrow + H_2$

ox

$Zn \rightarrow Zn^{2+} + 2\ e^-$

$2\ H^+ + 2\ e^- \rightarrow H_2$

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

$ZnCl_2 \rightarrow Zn^{2+} + 2\ Cl^-$

$Zn + 2\ H^+ \rightarrow Zn^{2+} + H_2$ ⇐ Forma ionica

$Zn + H^+ \rightarrow Zn^{2+} + H_2$

$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2$ ⇐ Forma molecolare

~~Cu + HCl~~

$Cu + HNO_3 \quad HNO_3 \rightarrow H^+ + NO_3^-$

red

$\overset{0}{Cu} + \overset{+5\ -2}{NO_3^-} + \overset{+1}{H^+} \rightarrow \overset{+2}{Cu^{2+}} + \overset{+2\ -2}{NO} + \overset{+1\ -2}{H_2O}$

ox

$Cu \rightarrow Cu^{2+} + 2\ e^-$ | x3

$\overset{+5}{NO_3^-} + 3\ e^- + 4\ H^+ \rightarrow \overset{+2}{NO} + 2\ H_2O$ | x2

$3\ Cu + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Cu^{2+} + 2\ NO + 4\ H_2O$

red

$\overset{+7\ -2}{MnO_4^-} + \overset{+1\ -2}{H_2S} + \overset{+1}{H^+} \rightarrow \overset{+2}{Mn^{2+}} + \overset{0}{S} + \overset{+1\ -2}{H_2O}$

ox

$\overset{-2}{H_2S} \rightarrow \overset{0}{S} + 2\ e^- + 2\ H^+$ | x5

$\overset{+7}{MnO_4^-} + 5\ e^- + 8\ H^+ \rightarrow \overset{+2}{Mn^{2+}} + 4\ H_2O$ | x2

$2\ MnO_4^- + 5\ H_2S + 16\ H^+ \rightarrow 2\ Mn^{2+} + 5\ S + 8\ H_2O + 10\ H^+$

$2\ MnO_4^- + 5\ H_2S + 6\ H^+ \rightarrow 2\ Mn^{2+} + 5\ S + 8\ H_2O$

red

$$\overset{+6\ -2}{Cr_2O_7^{2-}} + \overset{+2}{Fe^{2+}} + \overset{+1}{H^+} \rightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}} + \overset{+1\ -2}{H_2O}$$

ox

$2x+7(-2)=-2$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad | \times 6$$

$$\overset{+6}{Cr_2O_7^{2-}} + 6\,e^- + 14\,H^+ \rightarrow \overset{+3}{2\,Cr^{3+}} + 7\,H_2O$$

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

red

$$\overset{+7\ -2}{MnO_4^-} + \overset{-2}{S^{2-}} + \overset{+1\ -2}{H_2O} \rightarrow \overset{+4\ -2}{MnO_2} + \overset{0}{S} + \overset{-2\ +1}{OH^-}$$

ox

$$S^{2-} \rightarrow S + 2\,e^- \quad | \times 3$$

$$\overset{+7}{MnO_4^-} + 3\,e^- + 2\,H_2O \rightarrow \overset{+4}{MnO_2} + 4\,OH^- \quad | \times 2$$

$$2\,MnO_4^- + 3\,S^{2-} + 4\,H_2O \rightarrow 2\,MnO_2 + 3\,S + 8\,OH^-$$

$$2\,KMnO_4 + 3\,K_2S + 4\,H_2O \rightarrow 2\,MnO_2 + 3\,S + 8\,KOH$$

$$KMnO_4 + K_2S + H_2O \rightarrow MnO_2 + S + KOH$$

$$\overset{+7}{MnO_4^-} + 5\,e^- + 8\,H^+ \rightarrow \overset{+2}{Mn^{2+}} + 4\,H_2O$$

Titolazioni Redox

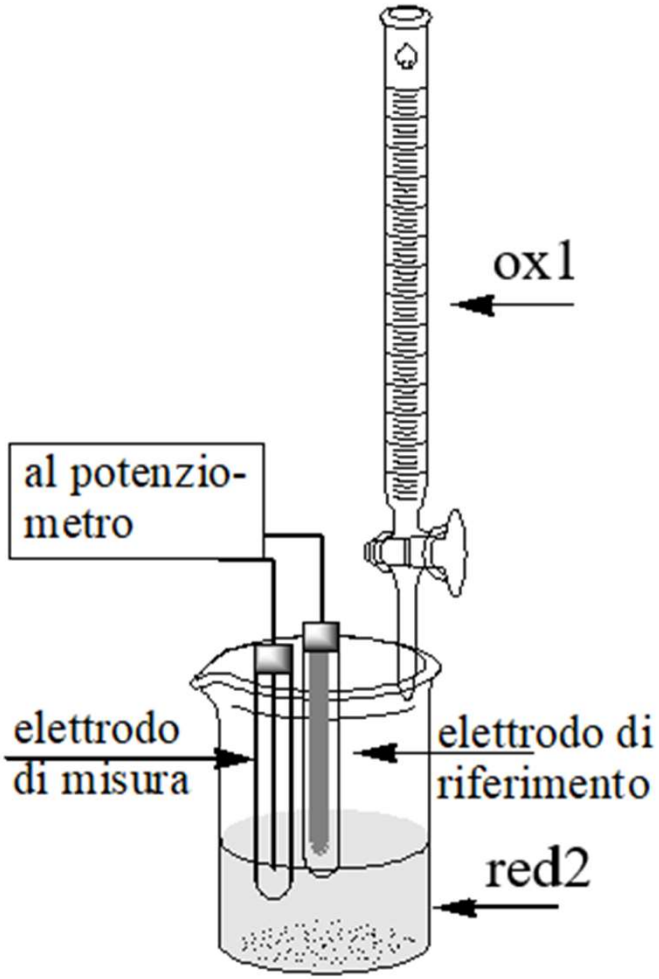
$ox_1 + ne^- \rightarrow red_1$

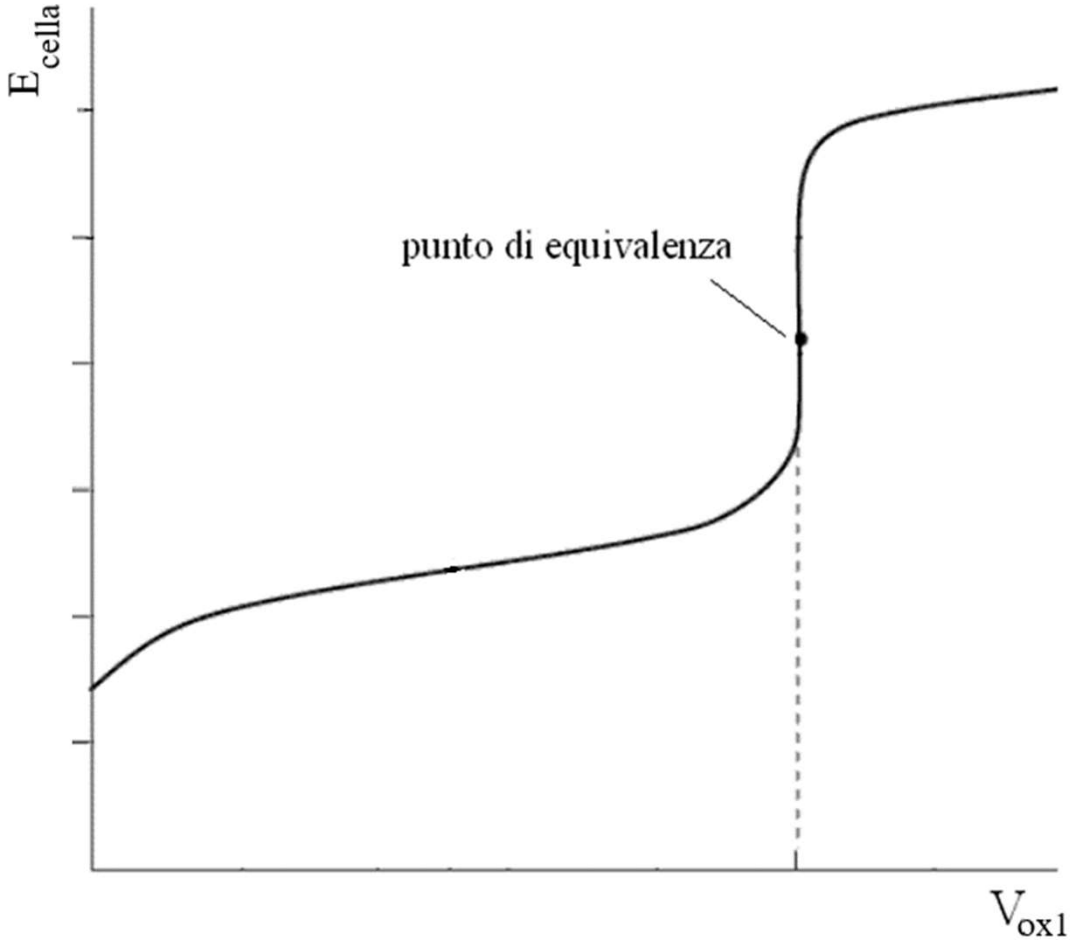
$red_2 \rightarrow ox_2 + ne^-$

$ox_1 + red_2 \rightarrow red_1 + ox_2$

$E°_1 > E°_2$

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$





Titolazioni Redox

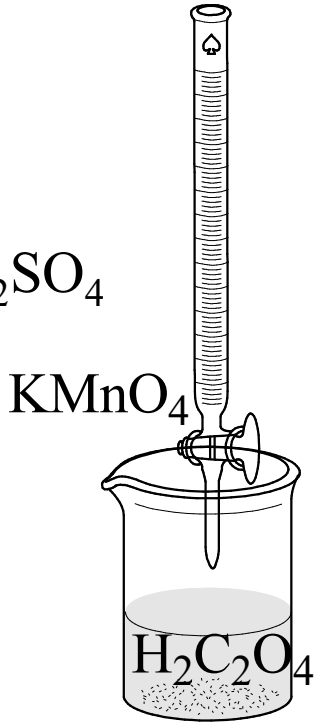
Esperienza n. 1: titolazione $H_2C_2O_4/KMnO_4$

$$\overset{+7}{MnO_4^-} + 5e^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O \qquad \times 2$$

$$\overset{+3}{H_2C_2O_4} \rightarrow 2\,\overset{+4}{CO_2} + 2e^- + 2\,H^+ \qquad \times 5$$

$$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ \rightarrow 2\,Mn^{2+} + 10\,CO_2\uparrow + 8\,H_2O$$

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 \rightarrow 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O + K_2SO_4$$



Red: $H_2C_2O_4$ $\qquad Peq_{Red} = \dfrac{PM_{Red}}{n_{e^-}} = \dfrac{PM_{Red}}{2}$

Ox: $KMnO_4$ $\qquad Peq_{Ox} = \dfrac{PM_{Ox}}{n_{e^-}} = \dfrac{PM_{Ox}}{5}$

In ambiente basico: $\overset{+7}{MnO_4^-} + 3e^- + 2\,H_2O \rightarrow \overset{+4}{MnO_2} + 4\,OH^-$

$neq_{Ox} = neq_{Red} \quad \Rightarrow N_{Ox}V_{Ox} = N_{Red}V_{Red}$

Determinazione COD (Chemical Oxygen Demand)

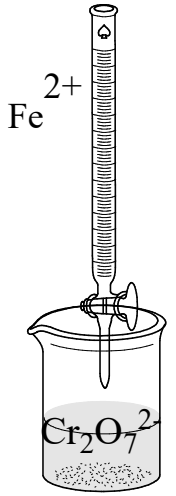
Ossidante: $E°_{Cr_2O_7^{2-}/Cr^{3+}} = 1{,}33$ V

Riducente: $E°_{Fe^{3+}/Fe^{2+}} = 0{,}77$ V

$Cr_2O_7^{2-} + 6\ e^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 7\ H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ x6

$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$

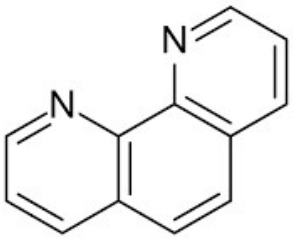


Retrotitolazione

Indicatori Redox

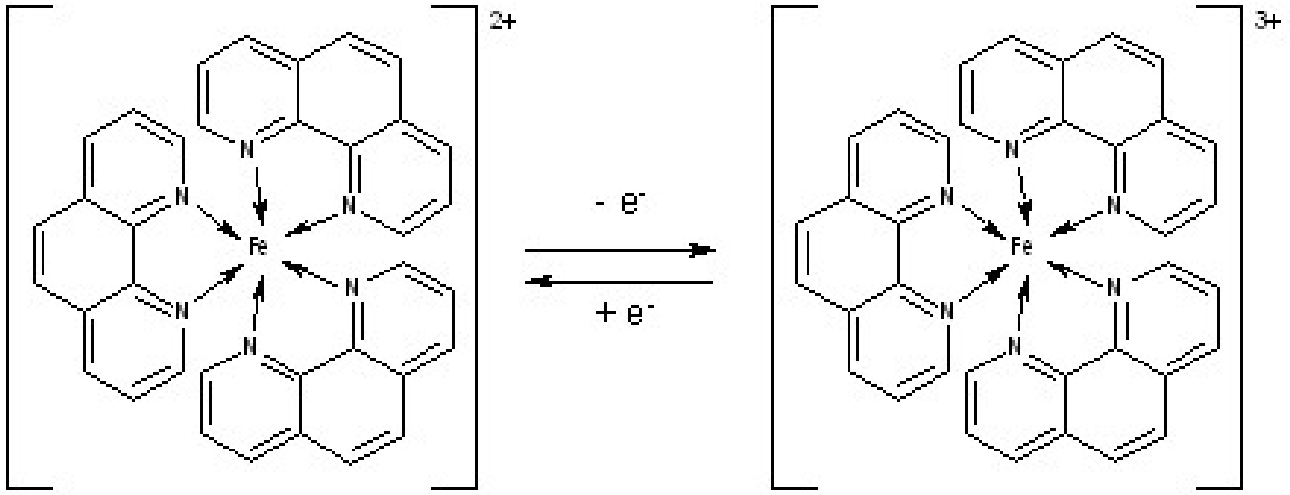
$Ind_{Ox} + ne^- \rightarrow Ind_{Red}$

col.1 col.2



1-10 fenantrolina

ferroina



Forma ridotta (rosso) Forma ossidata (azzurra)