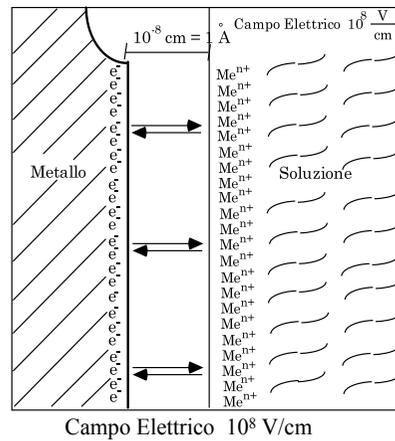
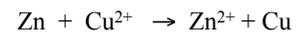
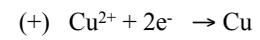
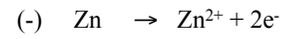
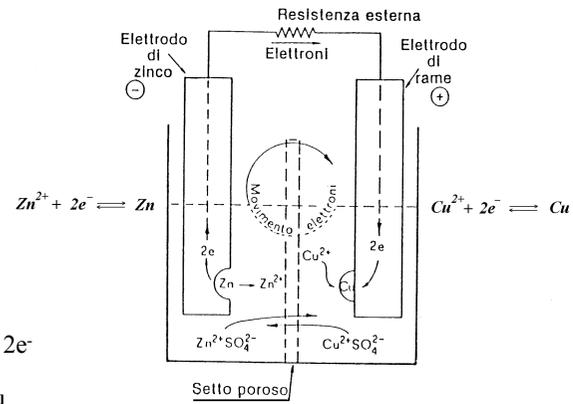


Gli atomi di zinco passano in soluzione come ioni Zn^{2+} idrati: $Zn \rightarrow Zn^{2+}_{aq} + 2e^-$; gli elettroni restano nel metallo e si crea un doppio strato elettrico fra l'elettrodo (carico negativamente per l'eccesso di elettroni) e la soluzione (carica positivamente per la presenza degli ioni Zn^{2+}).

Schematizzazione del doppio strato



- Capacità del doppio strato $C \approx 1 \mu F cm^{-2}$ per
 - d.d.p. di ≈ 1 Volt (questo è l'ordine di grandezza)
 - La carica Q del condensatore $Q = C V$ (coulomb cm^{-2}) $\approx 10^{-6} Q cm^{-2}$
 - 1 mole di elettroni = 96485 Coulomb
- (10^{-6} Coulomb $\approx 10^{-11}$ equivalenti \approx un milionesimo di mg)

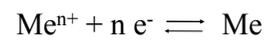
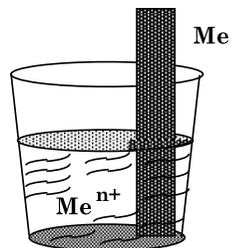


$$\Delta G < 0$$

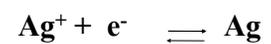
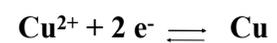
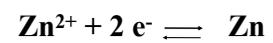
Quando $\Delta G = 0$ la pila è scarica

Figura - Schema di funzionamento di una pila elettrica a rame/zinco (J.F. Daniell; - 1820).

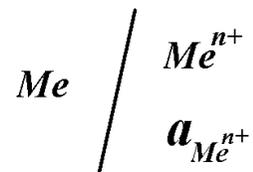
Semielementi di I° Specie



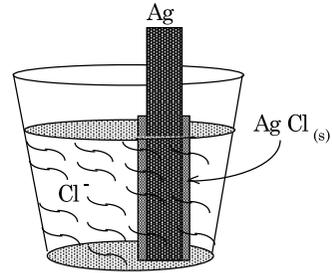
Esempi:



Schematizzazione dell'elettrodo



Semielementi di II° Specie

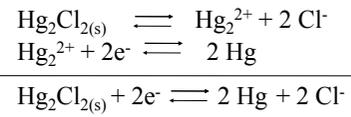


Schematizzazione dell'elettrodo

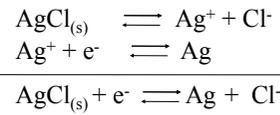
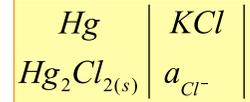
Me
+
Sale poco
solubile del Me

Soluzione di
elettrolita con
ione a comune
del sale poco
solubile del Me

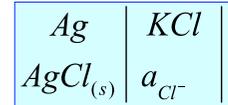
Esempi:



**Elettrodo a
calomelano**

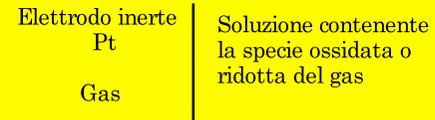


**Elettrodo di Arento-
Cloruro di argento**

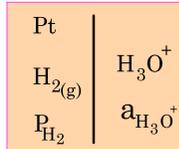
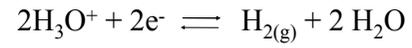


Semielementi a Gas

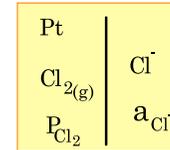
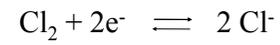
Schematizzazione dell'elettrodo



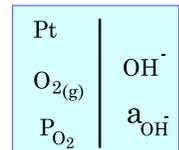
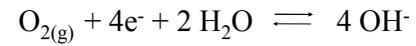
Esempio: elettrodo di Idrogeno



Esempio: elettrodo di Cloro



Esempio: elettrodo di Ossigeno

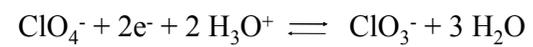


Semielementi di ossidoriduzione o REDOX

Schematizzazione dell'elettrodo

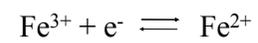
Elettrodo inerte Pt	Soluzione contenente una coppia redox
------------------------	--

Esempio:



Pt	ClO_4^- ClO_3^-
----	--------------------------------------

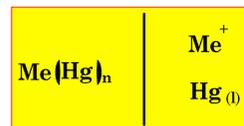
Esempio:



Pt	Fe^{3+} Fe^{2+}
----	--------------------------------------

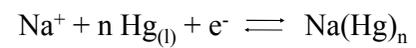
Semielemento ad amalgama

Schematizzazione dell'elettrodo



Elettrodo simile al semielemento di I° specie, la differenza consiste nell'attività del metallo che nell'amalgama non è unitaria.

Esempio:



Termodinamica del processo elettrochimico

La quantità massima di lavoro ottenibile da un sistema che evolve spontaneamente dallo stato iniziale allo stato finale è ricavabile, quando la trasformazione viene condotta attraverso un'infinita successione di stati d'equilibrio (trasformazione reversibile) come segue:

Dal I° principio della termodinamica per una trasformazione reversibile si ha:

$$\Delta U = Q_{\text{rev}} - L_{\text{rev}}$$

Poiché $\Delta H = \Delta U + P \Delta V$ si ha:

$$\Delta H - P \Delta V = Q_{\text{rev}} - L_{\text{rev}}$$

Dal II° principio della termodinamica $Q_{\text{rev}} = T \Delta S$

$$\Delta H - T \Delta S = -L_{\text{rev}} + P \Delta V$$

$$-\Delta G = L_{\text{utile massimo}}$$

Il lavoro elettrico è un lavoro utile

Il lavoro elettrico è definito come il prodotto di una quantità di carica per una differenza di potenziale (d.d.p.)

$$-\Delta G = L_{\text{elettrico}}$$

1 mol di elettroni = 96485 coulomb = 1 Faraday

$$-\Delta G = nF \Delta E$$

Equazione di Nernst

T = Costante

Per una generica reazione $\mathbf{aA + bB} \rightleftharpoons \mathbf{\gamma C + \delta D}$

$$\Delta G_{\text{reazione}} = \sum \nu_P \cdot \bar{G}_f(\text{Prodotti}) - \sum \nu_R \cdot \bar{G}_f(\text{Reagenti})$$

$$\bar{G}_i = \bar{G}_i^o + RT \ln a_i$$

$$\Delta G_{\text{reazione}} = \left(\gamma \bar{G}_C^o + RT \ln a_C^\gamma + \delta \bar{G}_D^o + RT \ln a_D^\delta \right) - \left(\alpha \bar{G}_A^o + RT \ln a_A^\alpha + \beta \bar{G}_B^o + RT \ln a_B^\beta \right)$$

$$\Delta G_{\text{reazione}} = \left[\left(\gamma \bar{G}_C^o + \delta \bar{G}_D^o \right) - \left(\alpha \bar{G}_A^o + \beta \bar{G}_B^o \right) \right] + RT \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta}$$

$$\Delta G_{\text{reazione}} = \Delta G_{\text{reazione}}^o + RT \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta}$$

Per una reazione di ossidoriduzione, in cui vi è un passaggio di elettroni dalla specie che si ossida a quella che si riduce, la variazione di energia libera può essere messa in relazione con il lavoro elettrico $\Delta G = - nF \Delta E$

$$\Delta G_{\text{reazione}} = \Delta G_{\text{reazione}}^{\circ} + RT \ln \frac{a_{\text{C}}^{\gamma} \cdot a_{\text{D}}^{\delta}}{a_{\text{A}}^{\alpha} \cdot a_{\text{B}}^{\beta}}$$

$$\Delta G = - nF \Delta E$$

$$\Delta E = - \frac{\Delta G^{\circ}}{nF} - \frac{RT}{nF} \ln \frac{a_{\text{C}}^{\gamma} \cdot a_{\text{D}}^{\delta}}{a_{\text{A}}^{\alpha} \cdot a_{\text{B}}^{\beta}}$$

Per una ben precisa reazione di ossidoriduzione, a T=cost, il n° di elettroni, che vengono scambiati sono determinati.

$$- \frac{\Delta G^{\circ}}{nF} = \Delta E^{\circ} \quad \text{Potenziale Standard}$$

$$\Delta E = \Delta E^{\circ} + \frac{RT}{nF} \ln \frac{a_{\text{A}}^{\alpha} \cdot a_{\text{B}}^{\beta}}{a_{\text{C}}^{\gamma} \cdot a_{\text{D}}^{\delta}}$$

Il ΔE in questa equazione è detta forza elettromotrice (f.e.m.) cioè la differenza di potenziale a circuito aperto (OCV)

$R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $T = 298.15 \text{ K}$; $F = 96485 \text{ Coulomb}$; $\ln = 2.3026 \log$

$$\Delta E = \Delta E^{\circ} + \frac{0.0591}{n} \log \frac{a_{\text{A}}^{\alpha} \cdot a_{\text{B}}^{\beta}}{a_{\text{C}}^{\gamma} \cdot a_{\text{D}}^{\delta}}$$

Equazione di Nernst

$$\Delta E = \Delta E^o + \frac{0.0591}{n} \log \frac{a_A^a \cdot a_B^b}{a_C^c \cdot a_D^d}$$

Quando $\Delta E = 0$ la reazione è all'equilibrio, in queste condizioni, si ha:

$$-\frac{n \Delta E^o}{0.0591} = \log \frac{a_A^a \cdot a_B^b}{a_C^c \cdot a_D^d} \quad \text{ovvero} \quad \frac{n \Delta E^o}{0.0591} = \log \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

$$\frac{n \Delta E^o}{0.0591} = \log K$$

$$K = 10^{\frac{n \Delta E^o}{0.0591}}$$

Vediamo una reazione reale



$$\Delta E = \Delta E^o + \frac{0.0591}{n} \log \frac{a_{\text{Cr}^{2+}} \cdot a_{\text{Fe}^{3+}}}{a_{\text{Cr}^{3+}} \cdot a_{\text{Fe}^{2+}}}$$

$$\frac{\Delta E^o}{0.0591} = \log \frac{a_{\text{Cr}^{3+}} \cdot a_{\text{Fe}^{2+}}}{a_{\text{Cr}^{2+}} \cdot a_{\text{Fe}^{3+}}}$$

Potenziale di un semielemento

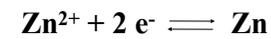
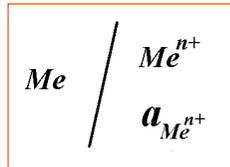
Ad ogni equilibrio chimico, in cui sono coinvolti elettroni, può essere applicata l'equazione di Nernst, quindi anche per l'equilibrio presente nel doppio strato elettrodo:

$$\alpha \text{Ox} + n e^- \rightleftharpoons \beta \text{Rid}$$

In cui Ox = forma ossidata, Rid = forma ridotta si ha:

$$E = E_{\text{Ox}/\text{Rid}}^{\circ} + \frac{0.0591}{n} \log \frac{a_{\text{Ox}}^{\alpha}}{a_{\text{Rid}}^{\beta}}$$

Esempio: elettrodi di I° specie



$$E = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

L'attività dei solidi e liquidi puri è unitaria $a_{\text{Zn}} = 1$

Esempio: elettrodi di II° specie

Me
+
Sale poco
solubile del Me

Soluzione di
elettrolita con
ione a comune
del sale poco
solubile del Me



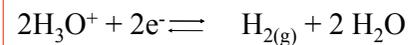
$$E = E_{\text{AgCl}_{(s)}/\text{Ag}}^{\circ} + \frac{0.0591}{1} \log \frac{a_{\text{AgCl}_{(s)}}}{a_{\text{Ag}} \cdot a_{\text{Cl}^-}}$$

L'attività dei solidi e liquidi puri è unitaria $a_{\text{AgCl}} = 1$; $a_{\text{Ag}} = 1$

Esempio: elettrodi a gas

Elettrodo inerte
Pt
Gas

Soluzione contenente
la specie ossidata o
ridotta del gas



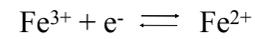
$$E = E_{\text{H}_3\text{O}^+/\text{H}_2}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} \cdot a_{\text{H}_2\text{O}}^2}$$

L'attività di un gas
(considerandolo ideale) = P

Esempio: elettrodi redox

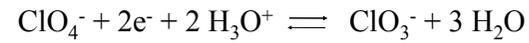
Elettrodo inerte
Pt

Soluzione contenente
una coppia redox



$$E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + \frac{0.0591}{1} \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

Altro esempio:



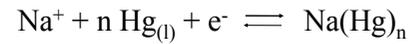
$$E = E_{\text{ClO}_4^-/\text{ClO}_3^-}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{ClO}_4^-} a_{\text{H}_3\text{O}^+}^2}{a_{\text{ClO}_3^-} a_{\text{H}_2\text{O}}^3}$$

L'attività dei liquidi puri
è unitaria $a_{\text{H}_2\text{O}} = 1$

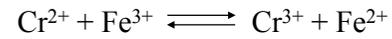
Esempio: elettro ad amalgama di sodio

Me(Hg)_n

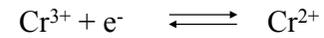
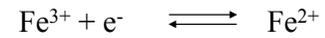
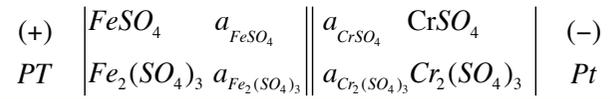
Me⁺
Hg_(l)



$$E = E_{\text{Na}^+/\text{Na}}^{\circ} + \frac{0.0591}{1} \log \frac{a_{\text{Na}^+} \cdot a_{\text{Hg}}^n}{a_{\text{Na}(\text{Hg})_n}}$$



$$\Delta E = \Delta E^\circ + \frac{0.0591}{n} \log \frac{a_{\text{Cr}^{2+}} \cdot a_{\text{Fe}^{3+}}}{a_{\text{Cr}^{3+}} \cdot a_{\text{Fe}^{2+}}}$$



$$E_{(+)} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ + \frac{0.0591}{1} \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

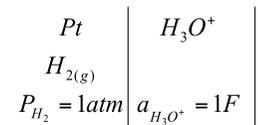
$$E_{(-)} = E_{\text{Cr}^{3+}/\text{Cr}^{2+}}^\circ + \frac{0.0591}{1} \log \frac{a_{\text{Cr}^{3+}}}{a_{\text{Cr}^{2+}}}$$

$$\Delta E = \text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \Delta E = \Delta E^\circ + \frac{0.0591}{1} \log \frac{a_{\text{Fe}^{3+}} a_{\text{Cr}^{2+}}}{a_{\text{Fe}^{2+}} a_{\text{Cr}^{3+}}}$$

Il potenziale standard E°

Elettrodo di idrogeno standard



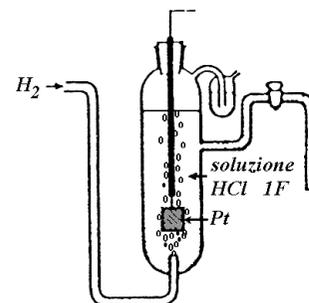
$$E = E_{H_3O^+/H_2}^\circ + \frac{0.0591}{2} \log \frac{a_{H_3O^+}^2}{a_{H_2} \cdot a_{H_2O}^2}$$

$$E = E_{H_3O^+/H_2}^\circ$$

Essendo l'argomento del logaritmo = 1

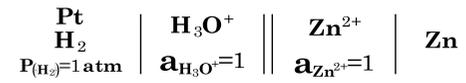
Per convenzione viene attribuito al potenziale di questo elettrodo il valore 0.000 V

In generale si definisce un elettrodo standard quando tutte le specie elettrochimicamente attive si trovano in condizione standard.



Determinazione dei potenziali standard

Si preparano delle pile con due elettrodi standard in cui uno di questi è l'elettrodo di idrogeno standard, per esempio:



si misura sperimentalmente per questa pila una f.e.m. 0.763 V

Se applico agli equilibri elettrodiici l'equazione di Nernst si ottiene:

$$\left| \begin{array}{l} 2 \text{H}_3\text{O}^+ + 2 e^- \rightleftharpoons \text{H}_{2(\text{g})} + 2 \text{H}_2\text{O} \\ E = E_{\text{H}_3\text{O}^+/\text{H}_2}^0 + \frac{0.059}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2}} \\ E_s = 0 \end{array} \right| \left| \begin{array}{l} \text{Zn}^{2+} + 2 e^- \rightleftharpoons \text{Zn} \\ E = E_{\text{Zn}^{2+}/\text{Zn}}^0 + \frac{0.059}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}} \\ E_d = E_{\text{Zn}^{2+}/\text{Zn}}^0 \end{array} \right|$$

La f.e.m. della pila deve essere sempre un valore positivo perché sia negativo il ΔG e quindi la reazione spontanea: f.e.m. = $E_{(+)} - E_{(-)}$

Determinazione della polarità della pila:

Metodi sperimentali

- Si controlla il verso della corrente
- Si controlla se c'è sviluppo di gas
- Se c'è consumo o aumento della massa di un elettrodo

Nel nostro caso, se si immerge dello zinco in acido, si osserva uno sviluppo spontaneo di gas e la massa dello zinco diminuisce questo significa che lo Zn si ossida e l' H_3O^+ si riduce.

$$\text{f.e.m.} = E_{(+)} - E_{(-)} = E_{(s)} - E_{(d)}$$

$$0.000 - E_{(d)} = 0.763$$

$$E_d = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = - 0.763 \text{ V}$$

Calcolo della polarità della pila:

Quando sono noti gli E° si applica l'equazione di Nernst e si calcolano direttamente i potenziali, quello con valore maggiore è il polo positivo.

Potenziale di un semielemento

TABELLA
Potenziali standard di riduzione, in soluzioni acquose, a 25°C (vol) (*).

$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3,045	$2\text{H}_2\text{SO}_3 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+0,40
$\text{K}^+ + e^- \rightleftharpoons \text{K}$	-2,925	$\rightleftharpoons \text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O}$	+0,401
$\text{Rb}^+ + e^- \rightleftharpoons \text{Rb}$	-2,925	$1/2\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightleftharpoons 2\text{OH}^-$	+0,401
$\text{Cs}^+ + e^- \rightleftharpoons \text{Cs}$	-2,923	$4\text{H}_2\text{SO}_3 + 4\text{H}_3\text{O}^+ + 6e^- \rightleftharpoons$	+0,51
$\text{Ba}^{2+} + 2e^- \rightleftharpoons \text{Ba}$	-2,90	$\rightleftharpoons \text{S}_2\text{O}_3^{2-} + 10\text{H}_2\text{O}$	+0,51
$\text{Sr}^{2+} + 2e^- \rightleftharpoons \text{Sr}$	-2,89	$\bullet \text{Cu}^+ + e^- \rightleftharpoons \text{Cu}$	+0,521
$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2,87	$\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$	+0,5355
$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	-2,714	$\text{Cu}^{2+} + \text{Cl}^- + e^- \rightleftharpoons \text{CuCl}$	+0,538
$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2,37	$\text{H}_3\text{AsO}_4 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+0,559
$\text{Lu}^{3+} + 3e^- \rightleftharpoons \text{Lu}$	-2,25	$\rightleftharpoons \text{HAsO}_2 + 4\text{H}_2\text{O}$	+0,554
$1/2\text{H}_2 + e^- \rightleftharpoons \text{H}^{\cdot}$	-2,25	$\text{MnO}_2 + e^- \rightleftharpoons \text{MnO}^{\cdot}$	+0,564
$\text{Sc}^{3+} + 3e^- \rightleftharpoons \text{Sc}$	-2,08	$\text{Cu}^+ + \text{Br}^- + e^- \rightleftharpoons \text{CuBr}$	+0,64
$\text{Be}^{2+} + 2e^- \rightleftharpoons \text{Be}$	-1,85	$\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+0,682
$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1,66	$\rightleftharpoons \text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$	+0,771
$\text{Ti}^{2+} + 2e^- \rightleftharpoons \text{Ti}$	-1,63	$\diamond \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0,771
$\text{Mn}^{2+} + 2e^- \rightleftharpoons \text{Mn}$	-1,18	$\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}$	+0,789
$\text{V}^{5+} + 2e^- \rightleftharpoons \text{V}$	$\approx -1,18$	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0,7991
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0,763	$\text{Cu}^{2+} + \text{I}^- + e^- \rightleftharpoons \text{CuI}$	+0,86
$\text{Cr}^{3+} + 3e^- \rightleftharpoons \text{Cr}$	-0,74	$2\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}_2^{2+}$	+0,920
$\text{Ga}^{3+} + 3e^- \rightleftharpoons \text{Ga}$	-0,53	$\text{NO}_2^- + 3\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+0,94
$\text{H}_3\text{PO}_4 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	-0,50	$\rightleftharpoons \text{HNO}_2 + 4\text{H}_2\text{O}$	+0,96
$\rightleftharpoons \text{H}_3\text{PO}_3 + 3\text{H}_2\text{O}$	-0,440	$\text{NO}_2^- + 4\text{H}_3\text{O}^+ + 3e^- \rightleftharpoons$	+1,0652
$\diamond \text{Fe}^{3+} + 2e^- \rightleftharpoons \text{Fe}$	-0,41	$\rightleftharpoons \text{NO} + 6\text{H}_2\text{O}$	+1,15
$\text{Cr}^{3+} + e^- \rightleftharpoons \text{Cr}^{2+}$	-0,41	$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1,15
$\text{Co}^{3+} + 2e^- \rightleftharpoons \text{Co}$	-0,403	$\text{SeO}_4^{2-} + 4\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+1,15
$\text{Ti}^{3+} + e^- \rightleftharpoons \text{Ti}^{2+}$	$\approx -0,37$	$\rightleftharpoons \text{H}_2\text{SeO}_3 + 5\text{H}_2\text{O}$	+1,15
$\text{In}^{3+} + 3e^- \rightleftharpoons \text{In}$	-0,342	$\text{IO}_2^- + 6\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	+1,195
$\text{Th}^{4+} + e^- \rightleftharpoons \text{Th}^{3+}$	-0,3363	$\rightleftharpoons 1/2\text{I}_2 + 9\text{H}_2\text{O}$	+1,229
$\text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co}$	-0,277	$\text{O}_2 + 4\text{H}_3\text{O}^+ + 4e^- \rightleftharpoons 6\text{H}_2\text{O}$	+1,25
$\text{H}_3\text{PO}_4 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	-0,276	$\text{Ti}^{3+} + 2e^- \rightleftharpoons \text{Ti}^+$	+1,25
$\rightleftharpoons \text{H}_3\text{PO}_3 + 3\text{H}_2\text{O}$	-0,255	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6e^- \rightleftharpoons$	+1,33
$\text{V}^{5+} + e^- \rightleftharpoons \text{V}^{4+}$	-0,250	$\rightleftharpoons 2\text{Cr}^{3+} + 2\text{H}_2\text{O}$	+1,3595
$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	-0,185	$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au}$	+1,50
$\text{CuI} + e^- \rightleftharpoons \text{Cu} + \text{I}^-$	-0,151	$\text{Mn}^{2+} + e^- \rightleftharpoons \text{Mn}^{+}$	+1,51
$\text{AgI} + e^- \rightleftharpoons \text{Ag} + \text{I}^-$	-0,136	$\text{MnO}_2 + 8\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	+1,51
$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0,126	$\rightleftharpoons \text{Mn}^{2+} + 12\text{H}_2\text{O}$	+1,52
$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	0,00	$\text{BrO}_2^- + 6\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	+1,61
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	+0,033	$\rightleftharpoons 1/2\text{Br}_2 + 9\text{H}_2\text{O}$	+1,68
$\text{CuBr} + e^- \rightleftharpoons \text{Cu} + \text{Br}^-$	+0,08	$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$	+1,61
$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{S}_2\text{O}_8^{2-}$	+0,137	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	$\approx +1,68$
$\text{CuCl} + e^- \rightleftharpoons \text{Cu} + \text{Cl}^-$	+0,15	$\text{MnO}_2 + 2\text{H}_3\text{O}^+ + 3e^- \rightleftharpoons$	+1,695
$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	+0,153	$\rightleftharpoons \text{MnO} + 4\text{OH}^-$	+1,77
$\bullet \text{Cu}^+ + e^- \rightleftharpoons \text{Cu}^{\cdot}$	+0,17	$\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons 4\text{H}_2\text{O}$	+1,82
$\text{SO}_4^{2-} + 4\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	+0,222 *	$\text{Ce}^{3+} + e^- \rightleftharpoons \text{Ce}^{2+}$	+1,98
$\rightleftharpoons \text{H}_2\text{SO}_3 + 5\text{H}_2\text{O}$	+0,2681 *	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+2,01
$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0,337 *	$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2,87
$\text{Hg}_2\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	+0,337	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	+0,36
$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu}$	+0,337		
$[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightleftharpoons$	+0,36		
$\rightleftharpoons [\text{Fe}(\text{CN})_6]^{2-}$			

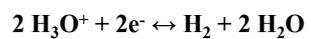
Tabella dei potenziali standard di semielementi (25°C) rispetto al SHE

$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3,045	$\text{CuBr} + e^- \rightleftharpoons \text{Cu} + \text{Br}^-$	+0,033	$\text{SeO}_4^{2-} + 4\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$	
$\text{K}^+ + e^- \rightleftharpoons \text{K}$	-2,925	$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{S}_2\text{O}_8^{2-}$	+0,08	$\rightleftharpoons \text{H}_2\text{SeO}_4 + 5\text{H}_2\text{O}$	+1,15
$\text{Rb}^+ + e^- \rightleftharpoons \text{Rb}$	-2,925	$\text{CuCl} + e^- \rightleftharpoons \text{Cu} + \text{Cl}^-$	+0,137	$\text{IO}_3^- + 6\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	
$\text{Cs}^+ + e^- \rightleftharpoons \text{Cs}$	-2,923	$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	+0,15	$\rightleftharpoons 1/2\text{I}_2 + 9\text{H}_2\text{O}$	+1,195
$\text{Ba}^{2+} + 2e^- \rightleftharpoons \text{Ba}$	-2,90	$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu}$	+0,153	$\text{O}_2 + 4\text{H}_3\text{O}^+ + 4e^- \rightleftharpoons 6\text{H}_2\text{O}$	+1,229
$\text{Sr}^{2+} + 2e^- \rightleftharpoons \text{Sr}$	-2,89	$\text{SO}_4^{2-} + 4\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$		$\text{Ti}^{3+} + 2e^- \rightleftharpoons \text{Ti}^+$	+1,25
$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2,87	$\rightleftharpoons \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$	+0,17	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6e^- \rightleftharpoons$	
$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	-2,714	$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	+0,222	$\rightleftharpoons 2\text{Cr}^{3+} + 21\text{H}_2\text{O}$	+1,33
$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2,37	$\text{Hg}_2\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	+0,2681	$\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1,3595
$\text{Lu}^{3+} + 3e^- \rightleftharpoons \text{Lu}$	-2,25	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0,337	$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au}$	+1,50
$1/2\text{H}_2 + e^- \rightleftharpoons \text{H}^-$	-2,25	$[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightleftharpoons$		$\text{Mn}^{3+} + e^- \rightleftharpoons \text{Mn}^{2+}$	+1,51
$\text{Sc}^{3+} + 3e^- \rightleftharpoons \text{Sc}$	-2,08	$\rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0,36	$\text{MnO}_2 + 8\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	
$\text{Be}^{2+} + 2e^- \rightleftharpoons \text{Be}$	-1,85	$2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2e^- \rightleftharpoons$		$\rightleftharpoons \text{Mn}^{2+} + 12\text{H}_2\text{O}$	+1,51
$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1,66	$\rightleftharpoons \text{S}_2\text{O}_8^{2-} + 5\text{H}_2\text{O}$	+0,40	$\text{BrO}_2^- + 6\text{H}_3\text{O}^+ + 5e^- \rightleftharpoons$	
$\text{Ti}^{2+} + 2e^- \rightleftharpoons \text{Ti}$	-1,63	$1/2\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightleftharpoons 2\text{OH}^-$	+0,401	$\rightleftharpoons 1/2\text{Br}_2 + 9\text{H}_2\text{O}$	+1,52
$\text{Mn}^{2+} + 2e^- \rightleftharpoons \text{Mn}$	-1,18	$4\text{H}_2\text{SO}_4 + 4\text{H}_3\text{O}^+ + 6e^- \rightleftharpoons$		$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$	+1,61
$\text{V}^{2+} + 2e^- \rightleftharpoons \text{V}$	-1,18	$\rightleftharpoons \text{S}_2\text{O}_8^{2-} + 10\text{H}_2\text{O}$	+0,51	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	+1,68
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0,763	$\text{Cu}^+ + e^- \rightleftharpoons \text{Cu}$	+0,521	$\text{MnO}_2 + 2\text{H}_2\text{O} + 3e^- \rightleftharpoons$	
$\text{Cr}^{3+} + 3e^- \rightleftharpoons \text{Cr}$	-0,74	$\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$	+0,5355	$\rightleftharpoons \text{MnO}_2 + 4\text{OH}^-$	+1,695
$\text{Ga}^{3+} + 3e^- \rightleftharpoons \text{Ga}$	-0,53	$\text{Cu}^{2+} + \text{Cl}^- + e^- \rightleftharpoons \text{CuCl}$	+0,538	$\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons 4\text{H}_3\text{O}^+$	+1,77
$\text{H}_2\text{PO}_4^- + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$		$\text{H}_3\text{AsO}_4 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$		$\text{Co}^{3+} + e^- \rightleftharpoons \text{Co}^{2+}$	+1,82
$\rightleftharpoons \text{H}_2\text{PO}_4^- + 3\text{H}_2\text{O}$	-0,50	$\rightleftharpoons \text{HAsO}_2 + 4\text{H}_2\text{O}$	+0,559	$\text{Ag}^{2+} + e^- \rightleftharpoons \text{Ag}^+$	+1,98
$\text{Fe}^{3+} + 2e^- \rightleftharpoons \text{Fe}$	-0,440	$\text{MnO}_2 + e^- \rightleftharpoons \text{MnO}_2^-$	+0,564	$\text{S}_2\text{O}_8^{2-} + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2,01
$\text{Cr}^{3+} + e^- \rightleftharpoons \text{Cr}^{2+}$	-0,41	$\text{Cu}^{2+} + \text{Br}^- + e^- \rightleftharpoons \text{CuBr}$	+0,64	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	+2,87
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	-0,403	$\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$			
$\text{Ti}^{3+} + e^- \rightleftharpoons \text{Ti}^{2+}$	-0,37	$\rightleftharpoons \text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$	+0,682		
$\text{In}^{3+} + 3e^- \rightleftharpoons \text{In}$	-0,342	$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0,771		
$\text{Ti}^+ + e^- \rightleftharpoons \text{Ti}$	-0,3363	$\text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}$	+0,789		
$\text{Co}^{3+} + 2e^- \rightleftharpoons \text{Co}$	-0,277	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0,7991		
$\text{H}_2\text{PO}_4^- + 2\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$		$\text{Cu}^{2+} + \text{I}^- + e^- \rightleftharpoons \text{CuI}$	+0,86		
$\rightleftharpoons \text{H}_2\text{PO}_3^- + 3\text{H}_2\text{O}$	-0,276	$2\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}_2^{2+}$	+0,920		
$\text{V}^{3+} + e^- \rightleftharpoons \text{V}^{2+}$	-0,255	$\text{NO}_2^- + 3\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons$			
$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	-0,250	$\rightleftharpoons \text{HNO}_2 + 4\text{H}_2\text{O}$	+0,94		
$\text{CuI} + e^- \rightleftharpoons \text{Cu} + \text{I}^-$	-0,185	$\text{NO}_2^- + 4\text{H}_3\text{O}^+ + 3e^- \rightleftharpoons$			
$\text{AgI} + e^- \rightleftharpoons \text{Ag} + \text{I}^-$	-0,151	$\rightleftharpoons \text{NO} + 6\text{H}_2\text{O}$	+0,96		
$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0,136	$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1,0652		
$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-0,126				
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0,00				

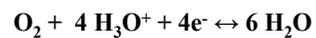
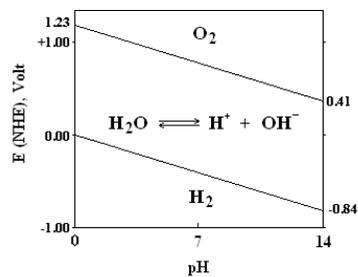
Tabella — Potenziali standard di semielementi in soluzione acquosa e a 25 °C, riferiti all'elettrodo standard di idrogeno (SHE, nota 25).

Semireazione	E_0 (V)	Semireazione	E_0 (V)
$Li^+ + e \rightleftharpoons Li$	-3,040	$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	0,081
$K^+ + e \rightleftharpoons K$	-2,931	$S + 2H_3O^+ + 2e \rightleftharpoons H_2S + 2H_2O$	0,142
$Ca^{2+} + 2e \rightleftharpoons Ca$	-2,868	$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} (HCl\ 1F)$	0,151
$Na^+ + e \rightleftharpoons Na$	-2,7108	$Cu^{+2} + e \rightleftharpoons Cu^+$	0,153
$Mg^{2+} + 2e \rightleftharpoons Mg$	-2,372	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	0,2681
$H_3O^+ + e \rightleftharpoons H_2O + H$	-2,10	$Cu^{2+} + 2e \rightleftharpoons Cu$	0,342
$Al^{3+} + 3e \rightleftharpoons Al$	-1,662	$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	0,401
$Ti^{2+} + 2e \rightleftharpoons Ti$	-1,630	$Cu^+ + e \rightleftharpoons Cu$	0,521
$ZnO_2^{2-} + 2H_2O + 2e \rightleftharpoons Zn + 4OH^-$	-1,215	$I_2 + 2e \rightleftharpoons 2I^-$	0,535
$Mn^{2+} + 2e \rightleftharpoons Mn$	-1,185	$O_2 + 2H_3O^+ + 2e \rightleftharpoons H_2O_2 + 2H_2O$	0,682
$Cr^{3+} + 2e \rightleftharpoons Cr$	-0,913	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	0,771
$2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$	-0,8277	$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	0,7973
$Te + 2H_3O^+ + 2e \rightleftharpoons H_2Te + 2H_2O$	-0,783	$Ag^+ + e \rightleftharpoons Ag$	0,7996
$Zn^{2+} + 2e \rightleftharpoons Zn$	-0,7618	$2NO_3^- + 4H_3O^+ + 2e \rightleftharpoons N_2O_5 + 6H_2O$	0,803
$Cr^{3+} + 3e \rightleftharpoons Cr$	-0,744	$NO_3^- + 3H_3O^+ + 2e \rightleftharpoons HNO_2 + 4H_2O$	0,934
$As + 3H_3O^+ + 3e \rightleftharpoons AsH_3 + 3H_2O$	-0,608	$NO_3^- + 4H_3O^+ + 3e \rightleftharpoons NO + 6H_2O$	0,957
$H_3PO_2 + H_3O^+ + e \rightleftharpoons P + 3H_2O$	-0,508	$Br_{2(l)} + 2e \rightleftharpoons 2Br^-$	1,065
$Fe^{2+} + 2e \rightleftharpoons Fe$	-0,447	$Pt^{2+} + 2e \rightleftharpoons Pt$	1,118
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	-0,407	$MnO_2 + 4H_3O^+ + 2e \rightleftharpoons Mn^{2+} + 6H_2O$	1,224
$Cd^{2+} + 2e \rightleftharpoons Cd$	-0,403	$O_2 + 4H_3O^+ + 4e \rightleftharpoons 6H_2O$	1,229
$Se + 2H_3O^+ + 2e \rightleftharpoons H_2Se + 2H_2O$	-0,400	$Cr_2O_7^{2-} + 14H_3O^+ + 6e \rightleftharpoons 2Cr^{3+} + 21H_2O$	1,232
$Tl^+ + e \rightleftharpoons Tl$	-0,336	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1,358
$Co^{2+} + 2e \rightleftharpoons Co$	-0,277	$ClO_2^- + 6H_3O^+ + 6e \rightleftharpoons Cl^- + 9H_2O$	1,451
$Ni^{2+} + 2e \rightleftharpoons Ni$	-0,257	$PbO_2 + 4H_3O^+ + 2e \rightleftharpoons Pb^{2+} + 6H_2O$	1,455
$Mo^{3+} + 3e \rightleftharpoons Mo$	-0,200	$MnO_2 + 8H_3O^+ + 3e \rightleftharpoons Mn^{2+} + 12H_2O$	1,507
$Sn^{2+} + 2e \rightleftharpoons Sn$	-0,1374	$HClO + H_3O^+ + e \rightleftharpoons \frac{1}{2}Cl_2 + 2H_2O$	1,611
$Pb^{2+} + 2e \rightleftharpoons Pb$	-0,1263	$H_2O_2 + 2H_3O^+ + 2e \rightleftharpoons 4H_2O$	1,776
$2H_3O^+ + 2e \rightleftharpoons H_2 + 2H_2O$	0	$Co^{3+} + e \rightleftharpoons Co^{2+} (H_2SO_4\ 2F)$	1,83
$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-$	0,01	$F_2 + 2e \rightleftharpoons 2F^-$	2,866

Diagrammi Potenziale pH (diagrammi di Pourbaix)



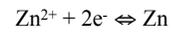
$$E = E_{\text{H}^+/\text{H}_2}^\circ + \frac{RT}{2F} \ln \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} \cdot a_{\text{H}_2\text{O}}} = E_{\text{H}^+/\text{H}_2}^\circ + \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+} - \frac{RT}{2F} \ln P_{\text{H}_2}$$



$$E = E_{\text{O}_2/\text{H}_2\text{O}}^\circ + \frac{RT}{4F} \ln \frac{a_{\text{O}_2} \cdot a_{\text{H}_3\text{O}^+}^4}{a_{\text{H}_2\text{O}}^6} = E_{\text{O}_2/\text{H}_2\text{O}}^\circ + \frac{RT}{F} \ln a_{\text{H}_3\text{O}^+} + \frac{RT}{4F} \ln P_{\text{O}_2}$$

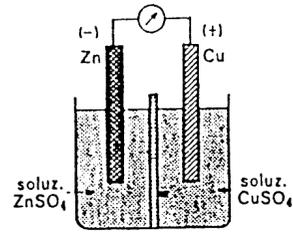
Esempio 1

Equilibrio elettrodo



Potenziale elettrodo

$$E_{(-)} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$



Schematizzazione della cella

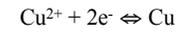


$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left(E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.0591}{2} \log a_{\text{Cu}^{2+}} \right) - \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a_{\text{Zn}^{2+}} \right)$$

$$\text{f.e.m.} = \left(E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} \right) + \frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Zn}^{2+}}}$$

Equilibrio elettrodo

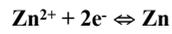


Potenziale elettrodo

$$E_{(+)} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}$$

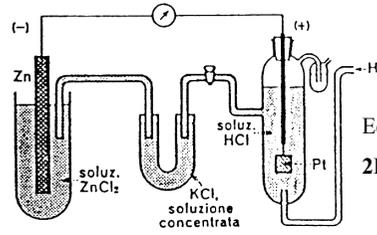
Esempio 2

Equilibrio elettrodo

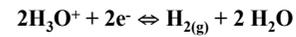


Potenziale elettrodo

$$E_{(-)} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$



Equilibrio elettrodo



Potenziale elettrodo

$$E_{(+)} = E_{\text{H}_3\text{O}^+/\text{H}_2}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} \cdot a_{\text{H}_2\text{O}}^2}$$

Schematizzazione della cella

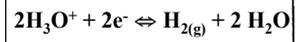
$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left(E_{\text{H}_3\text{O}^+/\text{H}_2}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} a_{\text{H}_2\text{O}}^2} \right) - \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a_{\text{Zn}^{2+}} \right)$$

$$\text{f.e.m.} = \left(E_{\text{H}_3\text{O}^+/\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} \right) + \left(\frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{Zn}^{2+}}} \right)$$

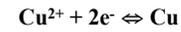
Esempio 3

Equilibrio elettrodoico

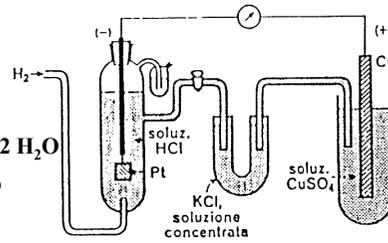


Potenziale elettrodoico

Equilibrio elettrodoico



Potenziale elettrodoico



$$E_{(-)} = E_{\text{H}_3\text{O}^+/\text{H}_2}^\circ + \frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} \cdot a_{\text{H}_2\text{O}}^2} \quad \boxed{\begin{array}{c|c|c} \text{Pt} & \text{H}_3\text{O}^+ & \text{CuSO}_4 \\ \text{H}_2 & a_{\text{H}_3\text{O}^+} & \\ \hline P_{\text{H}_2} = 1 \text{ atm} & & a_{\text{CuSO}_4} \end{array}} \quad E_{(+)} = E_{\text{Cu}^{2+}/\text{Cu}}^\circ + \frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}$$

Schematizzazione della cella

$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left(E_{\text{Cu}^{2+}/\text{Cu}}^\circ + \frac{0.0591}{2} \log a_{\text{Cu}^{2+}} \right) - \left(E_{\text{H}_3\text{O}^+/\text{H}_2}^\circ + \frac{0.0591}{2} \log \frac{a_{\text{H}_3\text{O}^+}^2}{a_{\text{H}_2} \cdot a_{\text{H}_2\text{O}}^2} \right)$$

$$\text{f.e.m.} = \left(E_{\text{Cu}^{2+}/\text{Cu}}^\circ - E_{\text{H}_3\text{O}^+/\text{H}_2}^\circ \right) + \left(\frac{0.0591}{2} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{H}_3\text{O}^+}^2} \right)$$

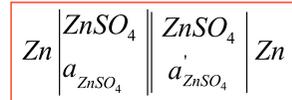
Pile a concentrazione

La f.e.m. di una pila è data dalla differenza di potenziale tra due elettrodi;

si dicono **pila chimiche** quando i due elettrodi sono diversi cioè su di essi avvengono due diverse reazioni elettrodiche;

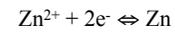
si dicono **pila a concentrazione** quando i due elettrodi sono uguali cioè sui due elettrodi avviene la stessa reazione elettrodica.

Esempio 1



In cui $a \neq a'$; supponiamo che $a' > a$

Equilibrio elettrodico



Potenziale elettrodico

$$E = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

$$\text{f.e.m.} = E_{(+)} - E_{(-)}$$

$$\text{f.e.m.} = \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a'_{\text{Zn}^{2+}} \right) - \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.0591}{2} \log a_{\text{Zn}^{2+}} \right)$$

$$\text{f.e.m.} = \frac{0.0591}{2} \log \frac{a'_{\text{Zn}^{2+}}}{a_{\text{Zn}^{2+}}}$$