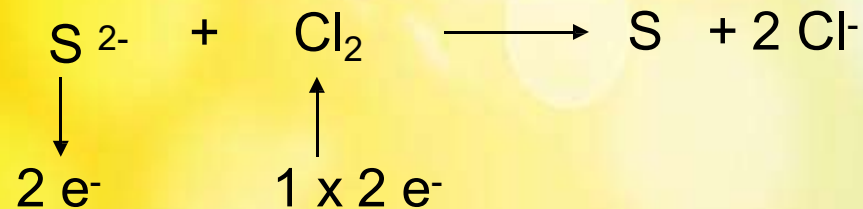
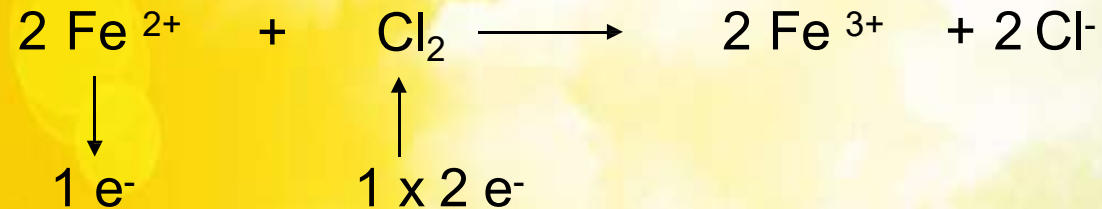
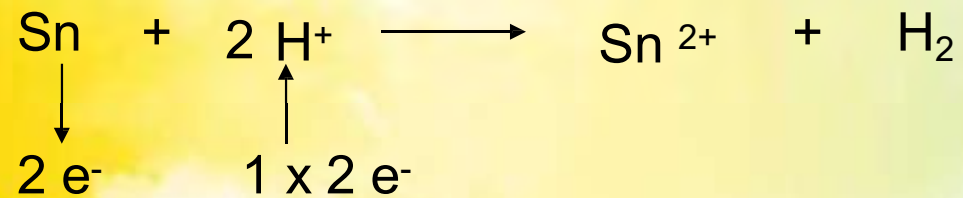
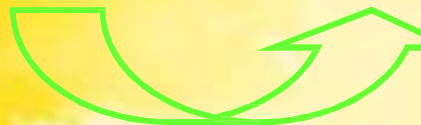


Reazioni di ossidoriduzione



numero di elettroni acquistati = numero di elettroni ceduti

OSSIDAZIONE



Avviene quando una specie cede elettroni

RIDUZIONE



Avviene quando una specie acquista elettroni

OSSIDANTI



specie che si riducono acquistano elettroni



diminuiscono il loro numero di ossidazione

RIDUCENTI

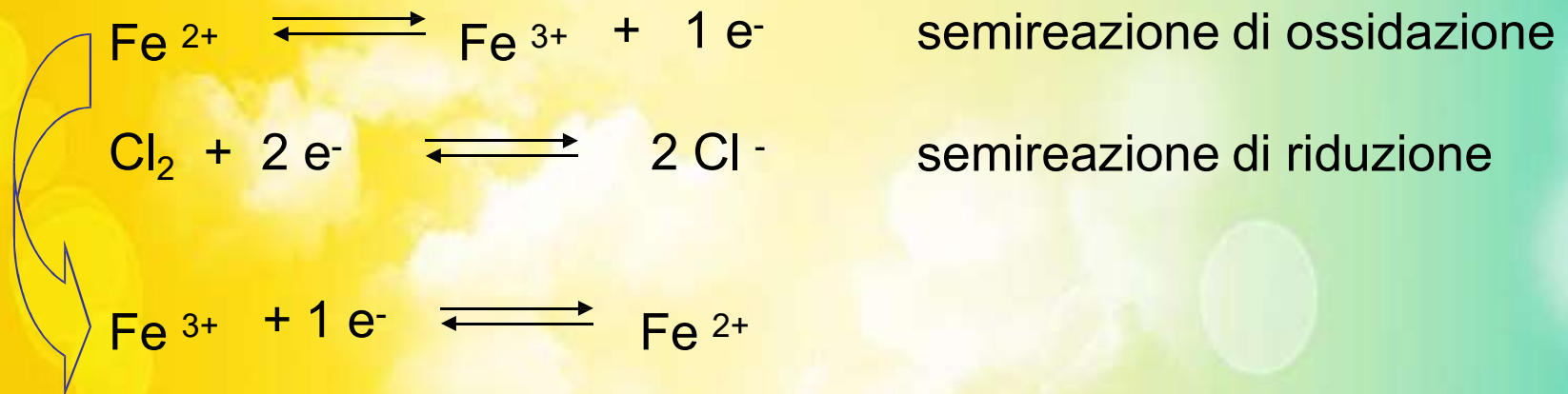


specie che si ossidano cedono elettroni



aumentano il loro numero di ossidazione

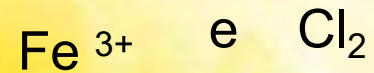
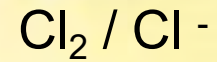
Ogni reazione redox può essere scritta come somma di due semireazioni



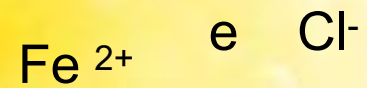
$\text{Fe}^{3+} / \text{Fe}^{2+}$

$\text{Cl}_2 / \text{Cl}^-$

Coppie redox coniugate



specie ossidate



specie ridotte

Ogni coppia redox presenta un particolare **potenziale redox E_0** determinato per confronto rispetto **all'elettrodo di riferimento di idrogeno in condizioni standard (valore 0)**

Temperatura

25°C

Concentrazione

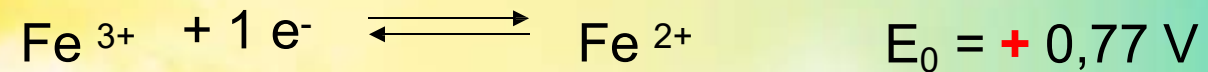
1 N

Pressione

1 atmosfera

Il potenziale redox può essere espresso come:

☀ Potenziale di riduzione

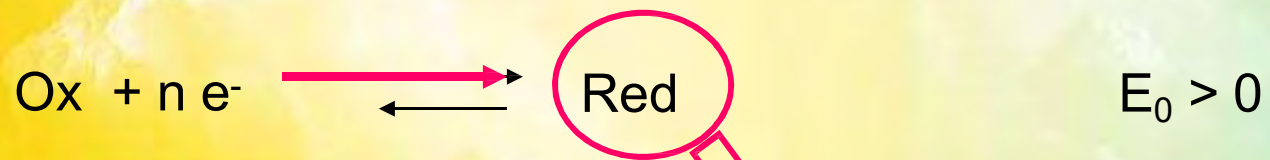


☀ Potenziale di ossidazione



Il segno del potenziale esprime la tendenza della reazione ad andare nel senso in cui è scritta

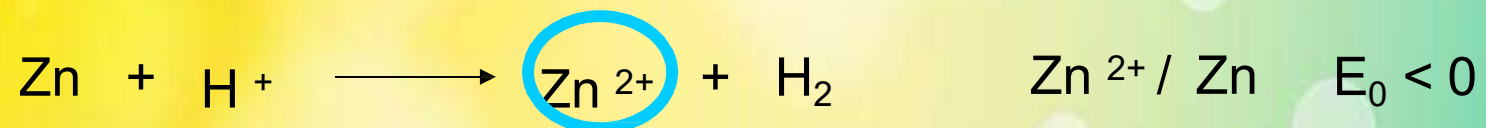
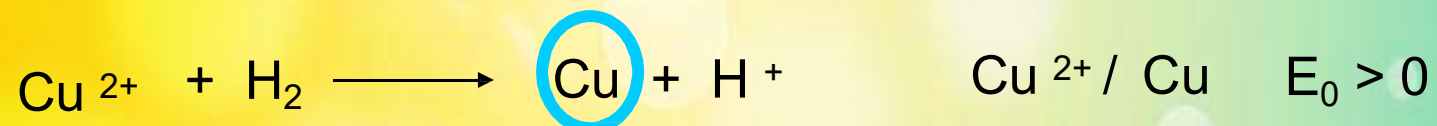
In generale:



Forma più stabile (H₂)



Forma più stabile (H₂)



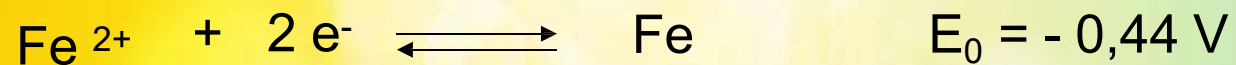
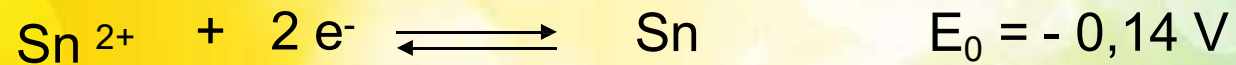
Reazioni	E_0 (V)	Reazioni	E_0 (V)
$Li^+ + e \rightleftharpoons Li$	- 3,045	$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	0,08
$K^+ + e \rightleftharpoons K$	- 2,924	$S + 2H_3O^+ + 2e \rightleftharpoons H_2S + 2H_2O$	0,14
$Ca^{2+} + 2e \rightleftharpoons Ca$	- 2,76	$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} (HCl \ 1F)$	0,15
$Na^+ + e \rightleftharpoons Na$	- 2,7109	$Cu^{2+} + e \rightleftharpoons Cu^+$	0,158
$Mg^{2+} + 2e \rightleftharpoons Mg$	- 2,375	$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$	0,2682
$H_3O^+ + e \rightleftharpoons H_2O + H$	- 2,10	$Cu^{2+} + 2e \rightleftharpoons Cu$	0,337
$Al^{3+} + 3e \rightleftharpoons Al$	- 1,71	$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$	0,401
$Ti^{2+} + 2e \rightleftharpoons Ti$	- 1,63	$Cu^+ + e \rightleftharpoons Cu$	0,521
$ZnO_2^{2-} + 2H_2O + 2e \rightleftharpoons Zn + 4OH^-$	- 1,22	$I_2 + 2e \rightleftharpoons 2I^-$	0,536
$Mn^{2+} + 2e \rightleftharpoons Mn$	- 1,03	$O_2 + 2H_3O^+ + 2e \rightleftharpoons H_2O_2 + 2H_2O$	0,682
$2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$	- 0,828	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	0,771
$Zn^{2+} + 2e \rightleftharpoons Zn$	- 0,7628	$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	0,7961
$Cr^{3+} + 3e \rightleftharpoons Cr$	- 0,74	$Ag^+ + e \rightleftharpoons Ag$	0,7996
$Te + 2H_3O^+ + 2e \rightleftharpoons H_2Te + 2H_2O$	- 0,72	$2NO_3^- + 4H_3O^+ + 2e \rightleftharpoons N_2O_4 + 6H_2O$	0,80
$As + 3H_3O^+ + 3e \rightleftharpoons AsH_3 + 3H_2O$	- 0,60	$NO_3^- + 3H_3O^+ + 2e \rightleftharpoons HNO_2 + 4H_2O$	0,94
$Cr^{2+} + 2e \rightleftharpoons Cr$	- 0,557	$NO_3^- + 4H_3O^+ + 3e \rightleftharpoons NO + 6H_2O$	0,96
$H_3PO_2 + H_3O^+ + e \rightleftharpoons P + 3H_2O$	- 0,51	$Br_2 + 2e \rightleftharpoons 2Br^-$	1,087
$Fe^{2+} + 2e \rightleftharpoons Fe$	- 0,409	$Pt^{2+} + 2e \rightleftharpoons Pt$	1,2
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	- 0,41	$MnO_2 + 4H_3O^+ + 2e \rightleftharpoons Mn^{2+} + 6H_2O$	1,21
$Cd^{2+} + 2e \rightleftharpoons Cd$	- 0,4026	$O_2 + 4H_3O^+ + 4e \rightleftharpoons 6H_2O$	1,229
$Se + 2H_3O^+ + 2e \rightleftharpoons H_2Se + 2H_2O$	- 0,40	$Cr_2O_7^{2-} + 14H_3O^+ + 6e \rightleftharpoons 2Cr^{3+} + 21H_2O$	1,33
$Tl^+ + e \rightleftharpoons Tl$	- 0,3363	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1,358
$Co^{2+} + 2e \rightleftharpoons Co$	- 0,277	$ClO_3^- + 6H_3O^+ + 6e \rightleftharpoons 6Cl^- + 9H_2O$	1,45
$Ni^{2+} + 2e \rightleftharpoons Ni$	- 0,230	$PbO_2 + 4H_3O^+ + 2e \rightleftharpoons Pb^{2+} + 6H_2O$	1,455
$N_2 + 5H_3O^+ + 4e \rightleftharpoons N_2H_5^+ + 5H_2O$	- 0,23	$MnO_4^- + 8H_3O^+ + 5e \rightleftharpoons Mn^{2+} + 12H_2O$	1,50
$Sn^{2+} + 2e \rightleftharpoons Sn$	- 0,1364	$HClO + H_3O^+ + e \rightleftharpoons \frac{1}{2}Cl_2 + 2H_2O$	1,63
$Pb^{2+} + 2e \rightleftharpoons Pb$	- 0,1263	$H_2O_2 + 2H_3O^+ + 2e \rightleftharpoons 4H_2O$	1,776
$2H_3O^+ + 2e \rightleftharpoons H_2 + 2H_2O$	0,000	$Co^{3+} + e \rightleftharpoons Co^{2+} (HNO_3 \ 3F)$	1,842
$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-$	0,0	$F_2 + 2e \rightleftharpoons 2F^-$	2,87

$$\Delta G = -n F \Delta E$$



$$\Delta G < 0$$


$$\Delta E > 0$$



$$\Delta E = E_{0 \text{ Sn}^{2+} / \text{Sn}} - E_{0 \text{ Fe}^{2+} / \text{Fe}}$$

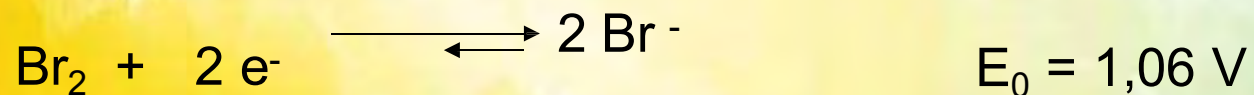
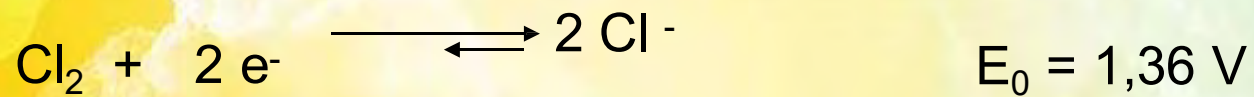
$$\Delta E = E_{0 \text{ Sn}^{2+} / \text{Sn}} - E_{0 \text{ Fe}^{2+} / \text{Fe}}$$

$$\Delta E = -0,14 - (-0,44) = 0,3 \text{ V}$$

$$\Delta E > 0$$

$$\Delta G < 0$$

Reazione spontanea



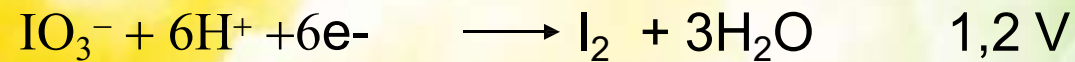
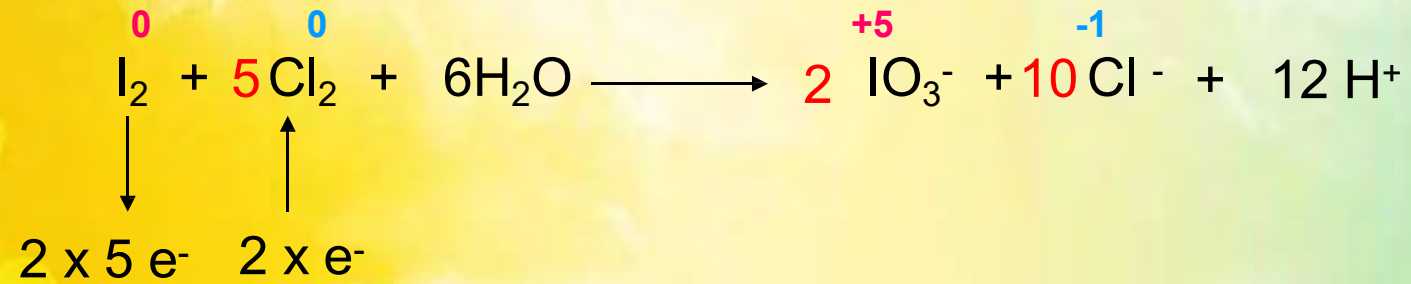
$$\Delta E = 1,36 - 1,06 = 0,3 \text{ V}$$



$$\Delta E = 1,36 - 0,51 = 0,85 \text{ V}$$

Tende ad avvenire prima la reazione per cui il ΔE risulta più elevato

In eccesso di acqua di cloro:



$$\Delta E = 1,36 - 1,2 = 0,16 \text{ V}$$

Se presente anche il bromo, rilevabile per comparsa colorazione bruna

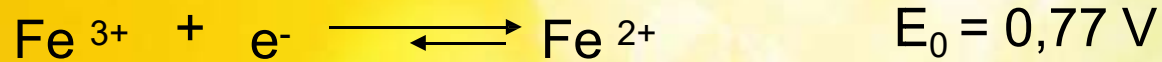
FATTORI CHE INFLUENZANO IL POTENZIALE

concentrazione

Equazione di Nernst

Potenziale attuale

$$E = E_0 + \frac{0,059}{n} \cdot \log \frac{[\text{Ox}]}{[\text{Rid}]}$$



$$E = 0,77 + \frac{0,059}{1} \cdot \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

Se $[Fe^{3+}] \gg [Fe^{2+}]$

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = 10^3$$

$$E = 0,77 + \frac{0,059}{1} \cdot \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$E = 0,77 + \frac{0,059}{1} \cdot \log 10^3$$

$$E_a = 0,77 + 0,059 \cdot 3 \cong 0,95 \text{ V}$$

Se $[Fe^{3+}] \ll [Fe^{2+}]$

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = 10^{-3}$$

$$E_a = 0,77 + 0,059 \cdot (-3) \cong 0,59 \text{ V}$$

In generale:

-all'aumentare della concentrazione della specie ossidante, aumentano le proprietà ossidanti

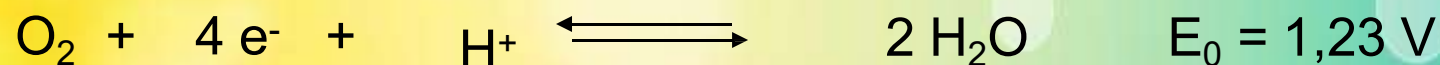
-all'aumentare della concentrazione della specie riducente, aumentano le proprietà riducenti

Al limite $E_a = \infty$ ma non esiste un ossidante tanto forte da ossidare completamente una specie coinvolta in un equilibrio

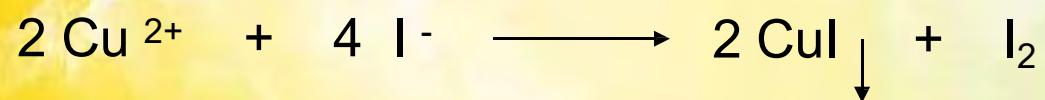
Esisterà sempre l'equilibrio



In soluzione acquosa il limite sarà posto da



Esempio



Avviene?????



$$E_0 = 0,15 \text{ V}$$



$$E_0 = 0,53 \text{ V}$$

$$\Delta E = 0,15 - 0,53 = -0,38$$

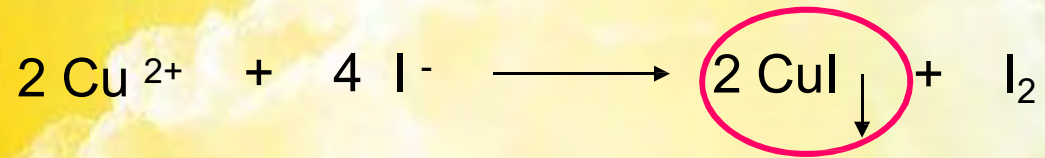
$\Delta G > 0$ non dovrebbe avvenire

ma poiché

H₂

Cu

I₂



$$E = 0,15 + \frac{0,059}{1} \cdot \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]}$$



$$K_s = [\text{Cu}^+][\text{I}^-]$$

$$\frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \gg 1$$

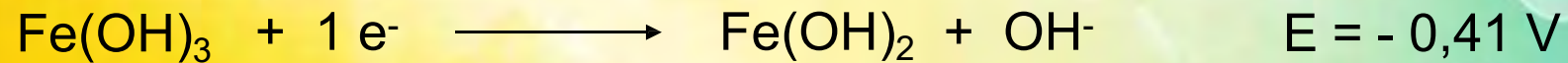
$$E > E_0 \quad (0.15)$$

$$E > 0,53$$



Esempio

In ambiente basico



$$E = E_0 + \frac{0,059}{1} \cdot \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

PH

$$K_{S_{\text{Fe}(\text{OH})_3}} = [\text{Fe}^{3+}] [\text{OH}^{-}]^3 = 10^{-35}$$

$$K_{S_{\text{Fe}(\text{OH})_2}} = [\text{Fe}^{2+}] [\text{OH}^{-}]^2 = 10^{-16}$$

$$[\text{Fe}^{3+}] = ?$$

$$[\text{Fe}^{2+}] = ?$$

$$\text{pH} = 14$$

$$[\text{OH}^-] = 1$$

$$K_{\text{S}_{\text{Fe}(\text{OH})_3}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 10^{-35}$$

$$K_{\text{S}_{\text{Fe}(\text{OH})_2}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 10^{-16}$$

$$[\text{Fe}^{3+}] = 10^{-35}$$

$$[\text{Fe}^{2+}] = 10^{-16}$$

$$E = E_0 + \frac{0,059}{1} \cdot \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E = 0,77 + \frac{0,059}{1} \cdot \log \frac{[10^{-35}]}{[10^{-16}]}$$

$$E = -0,41 \text{ V}$$

Riesco a sciogliere i metalli riducenti in ambiente acido



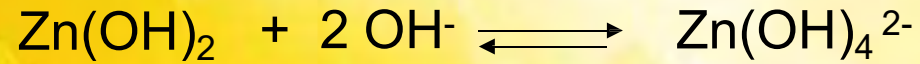
... e in ambiente basico?????

$$E = -0,76 + \frac{0,059}{2} \cdot \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}]}$$



$$K_s = [\text{Zn}^{2+}] [\text{OH}^-]^2 = 10^{-15}$$

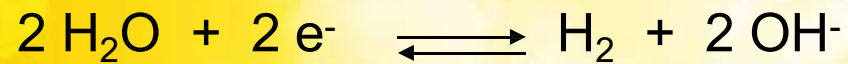
. . e in ambiente fortemente basico?????



$$E_0 = -1,22 \text{ V}$$



$$K_{\text{inst}} = \frac{[\text{Zn}^{2+}][\text{OH}^-]^4}{[\text{Zn(OH)}_4^{2-}]} = 10^{-30}$$



$$E = -0,83 \text{ V}$$

Acqua come ossidante

Il potenziale redox può essere influenzato dal pH

Acqua come OSSIDANTE



$$E = -0,83 \text{ V}$$

In ambiente basico



$$E = 0,00 \text{ V} \quad \text{In ambiente acido}$$

$$E = 0 + \frac{0,059}{2} \log \frac{[\text{H}^+]^2}{[\text{H}_2]}$$

$$p_{\text{H}_2} = 1$$

$$E = 0 + 0,059 \log [\text{H}^+]$$

Se pH = 14

$$E = 0 + 0,059 \log 10^{-14}$$

$$E = -0,826 \text{ V}$$

Il potenziale redox può essere influenzato dal pH



$$E = E_0 + \frac{0,059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

$$E = 1,51 + \frac{0,059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} + 8 \cdot \frac{0,059}{5} \log [\text{H}^+]$$

$$[\text{MnO}_4^-] = [\text{Mn}^{2+}]$$

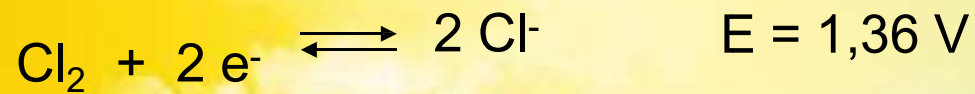
$$E = 1,51 + 0,09 \log [\text{H}^+] = 1,51 - 0,09 \text{ pH}$$

pH = 0 \longrightarrow E = 1,51 V

pH = 3 \longrightarrow E = 1,24 V

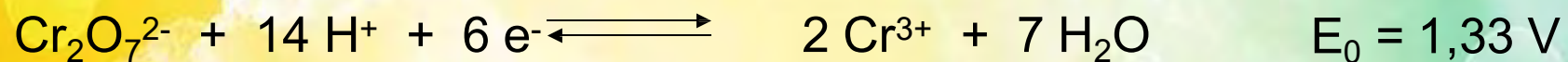
pH = 5 \longrightarrow E = 1,06 V

$$E = 1,51 - 0,09 \text{ pH}$$



$\Delta E > 0$ $\left\{ \begin{array}{l} 1,36 = 1,51 - 0,09 \text{ pH} \\ 1,06 = 1,51 - 0,09 \text{ pH} \\ 0,51 = 1,51 - 0,09 \text{ pH} \end{array} \right.$





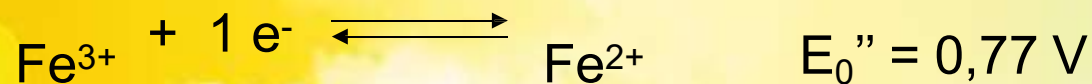
$$E = E_0 + \frac{0,059}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2}$$

$$E = 1,33 + \frac{0,059}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2} + 14 \cdot \frac{0,059}{6} \log [\text{H}^+]$$

$$[\text{Cr}_2\text{O}_7^{2-}] = [\text{Cr}^{3+}]$$

$$E = 1,33 - 0,14 \text{ pH}$$

Potenziale redox e K eq



$$K_{eq} = \frac{[\text{Sn}^{4+}][\text{Fe}^{2+}]^2}{[\text{Sn}^{2+}][\text{Fe}^{3+}]^2}$$

All'equilibrio $E' = E''$

$$0,77 + \frac{0,059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0,15 + \frac{0,059}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]}$$

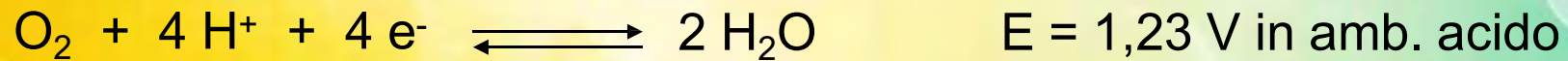
$$0,77 - 0,15 = \frac{0,059}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]} - \frac{0,059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$0,77 - 0,15 = \frac{0,059}{2} \log \frac{[\text{Sn}^{4+}] [\text{Fe}^{2+}]^2}{[\text{Sn}^{2+}] [\text{Fe}^{3+}]^2} = 20$$

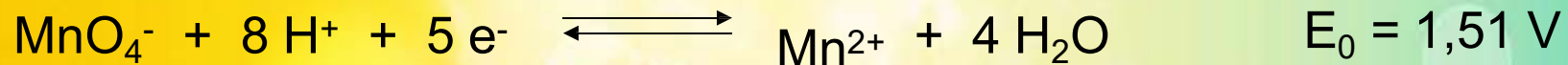
$$0,62 = \frac{0,059}{2} \log K_{\text{eq}} \cong 20$$

$$K_{\text{eq}} \cong 10^{20}$$

Acqua come RIDUCENTE



Non esiste libero in soluzione



Possibile ma cinematicamente sfavorita

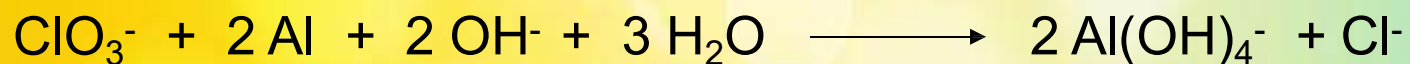
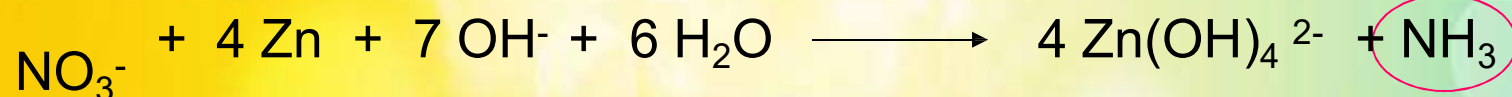
Soluzioni di Permanganato molto stabili in acqua

RIDUCENTI

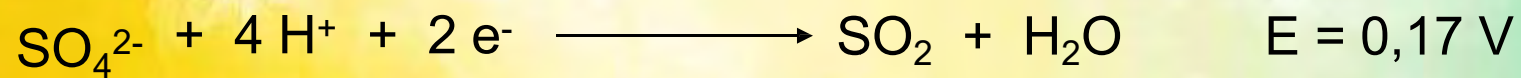
Metalli riducenti

Zn Al

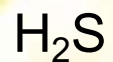
Lega di Devarda



Anidride solforosa



Acido solfidrico



OSSIDANTI

Alogeni

HNO_3

Acqua regia

H_2SO_4 concentrato

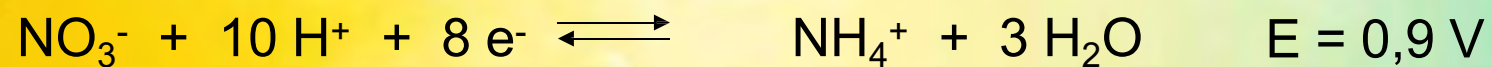
H_2O_2

KMnO_4

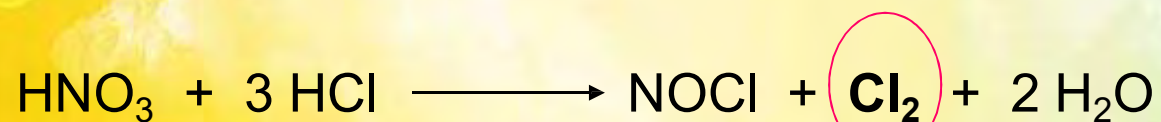
$\text{K}_2\text{Cr}_2\text{O}_7$

MnO_2 , PbO_2

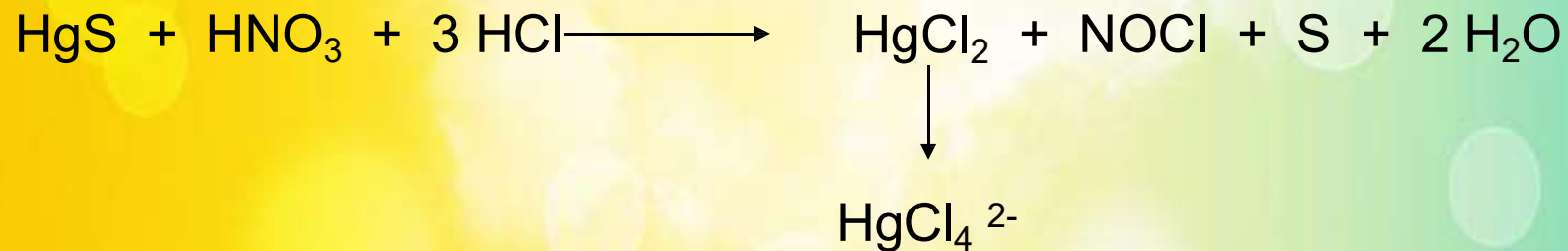
HNO₃



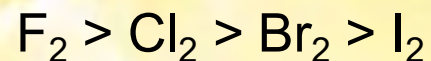
Acqua regia



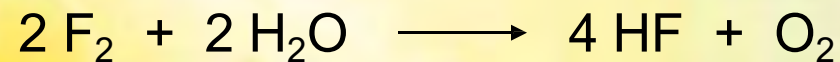
ha potenziale > del teorico



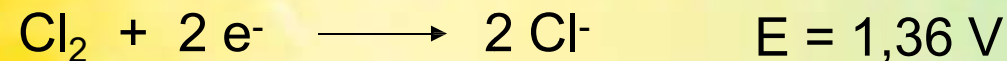
Alogeni



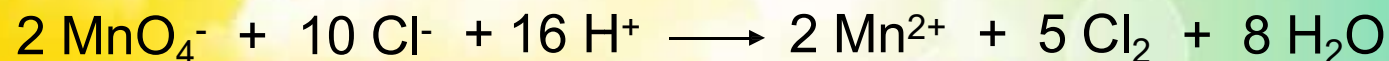
Fluoro



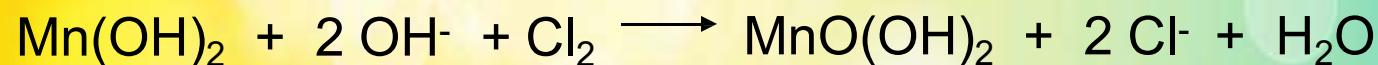
Cloro



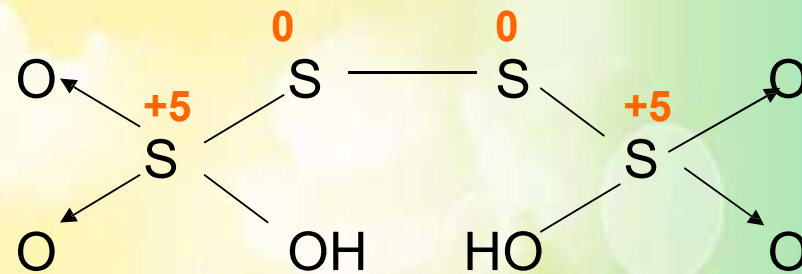
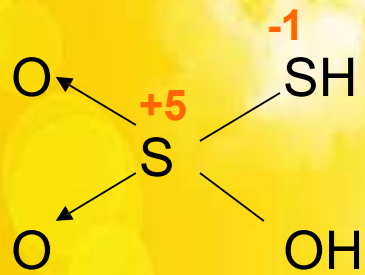
ambiente acido



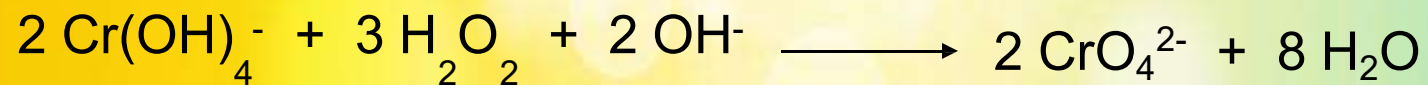
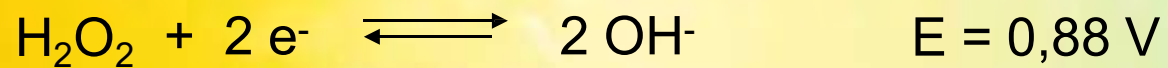
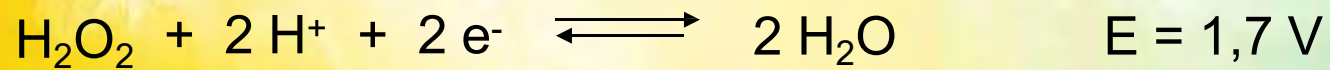
ambiente basico



Iodio



H₂O₂



KMnO₄

