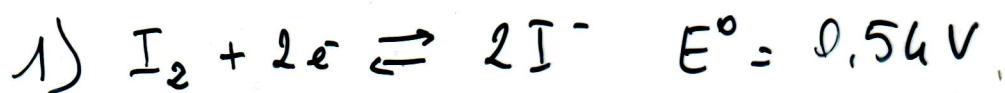
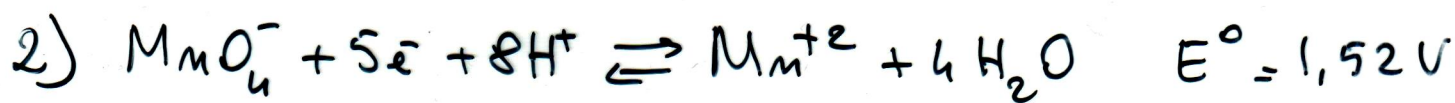


## 5. INFLUENZA DEL pH SUGLI EQUILIBRI REDOX

Consideriamo vari tipi di equilibri Redox:

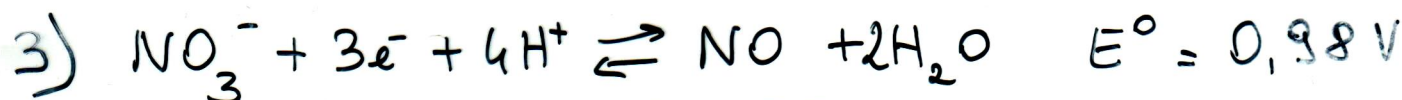


$$E = E^\circ + \frac{0,06}{2} \log \frac{[I_2]}{[I^-]^2} = E^\circ - 0,03 \log [I^-]^2$$



$$E = E^\circ + \frac{0,06}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

$$E = E^\circ + \frac{0,06}{5} \log \frac{[MnO_4^-]}{[Mn^{+2}]} + \frac{0,06}{5} \log [H^+]^8$$



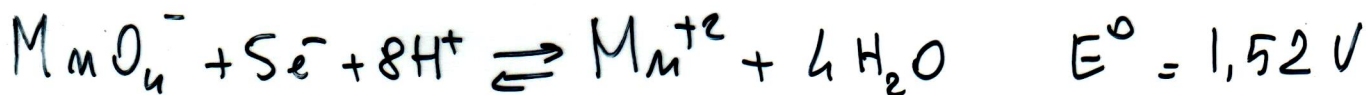
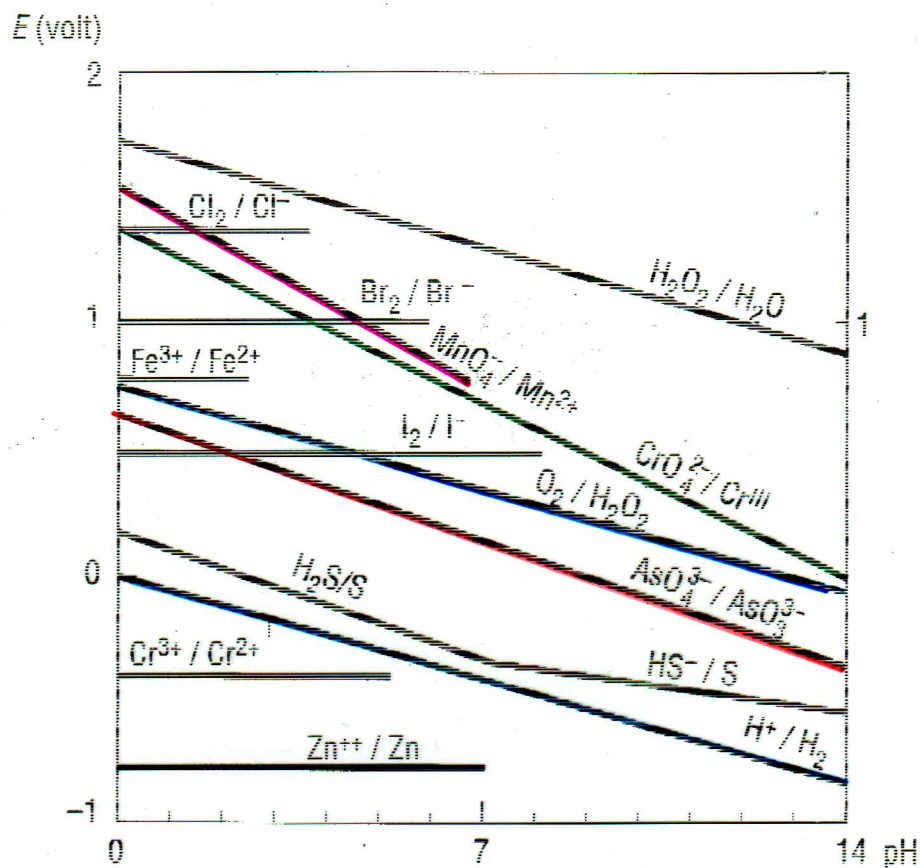
$$E = E^\circ + \frac{0,06}{3} \log \frac{[NO_3^-][H^+]^4}{[NO]}$$

$$E = E^\circ + 0,02 \log [NO_3^-] + 0,02 \log [H^+]^4$$

Il potenziale per un generico **OSSIDANTE OSSIGENATO**, per il bilanciamento delle cui semireazioni saranno **SEMPRE** necessari ioni  $H^+$ , sarà espresso dalla formula:

$$E = E^\circ + \frac{0,06}{n} \log \frac{[ox]}{[red]} - \frac{0,06 \cdot m}{n} pH$$

Il potenziale di queste specie è sempre **INVERSAMENTE** PROPORZIONALE al pH.



$$E = E^\circ + \frac{0,06}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} + \frac{0,06}{5} \log [\text{H}^+]^8$$

$$E = E^\circ + \frac{0,06}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} + 0,096 \log [\text{H}^+]$$

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

$$E = E^\circ - 0,096 \text{ pH} = 1,52 - 0,096 \text{ pH}$$

$$\text{pH} = 0 \quad E = E^\circ = 1,52 \text{ V}$$

$$\text{pH} = 3 \quad E = 1,52 - 0,29 = 1,23 \text{ V}$$

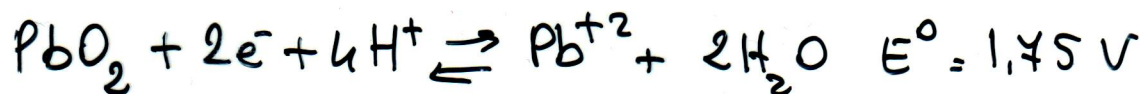
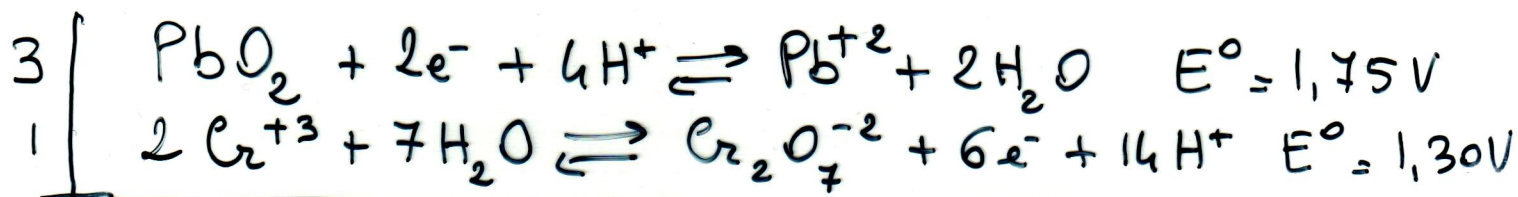
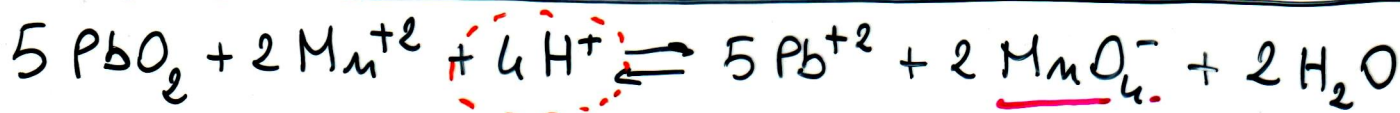
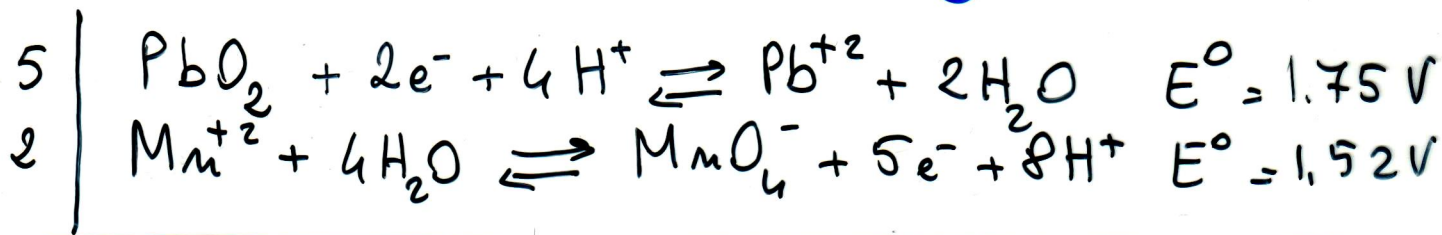
$$\text{pH} = 5 \quad E = 1,52 - 0,48 = 1,04 \text{ V}$$

$$\text{pH} = 7 \quad E = 1,52 - 0,67 = 0,85 \text{ V}$$

$$\text{pH} = 10 \quad E = 1,52 - 0,96 = 0,56 \text{ V}$$



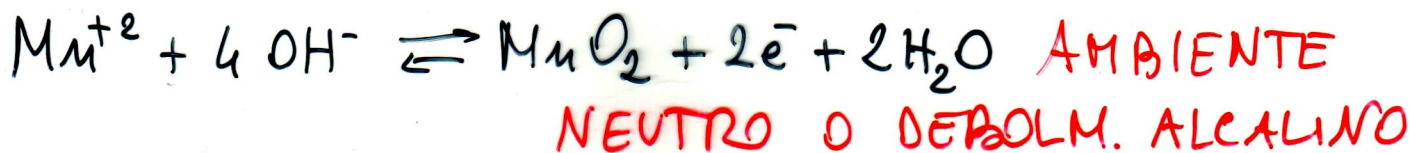
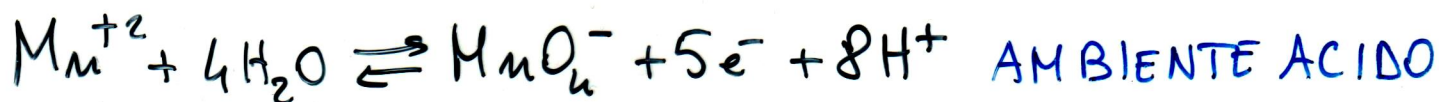
# ESEMPIO I $\equiv$ OSSIDAZIONE DEL $Mn^{+2}$ E $Cr^{+3}$ CON $PbO_2$



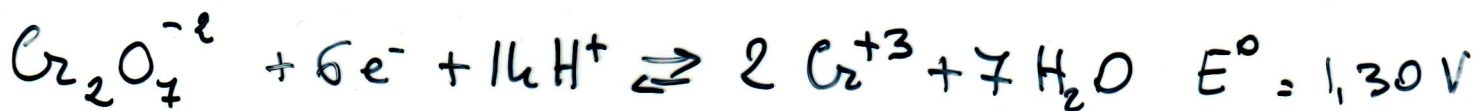
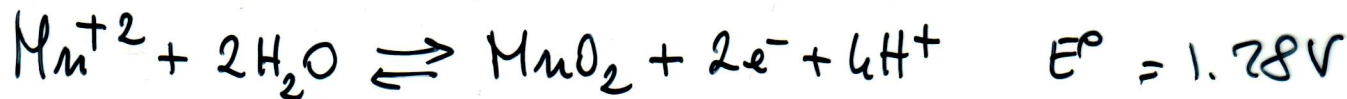
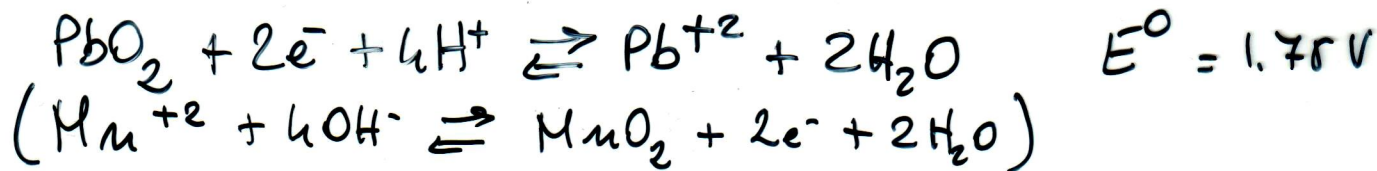
$$E = E^0 + \frac{0.06}{2} \log \frac{[PbO_2][H^+]^4}{[Pb^{+2}]} = E^0 + \frac{0.06}{2} \log [H^+]^4$$

$$E = E^0 - 0.12 \text{ pH} = 1.75 - 0.12 \text{ pH}$$

	$PbO_2 / Pb^{+2}$	$MnO_4^- / Mn^{+2}$	$\Delta E$
$pH = 0$	$E = 1.75V$	$E = 1.52V$	0.23
$pH = 3$	$E = 1.39V$	$E = 1.23V$	0.16
$pH = 5$	$E = 1.15V$	$E = 1.04V$	0.11
$pH = 10$	$E = 0.55V$	$E = 0.56V$	0.01



$$a \text{ pH} > 3$$



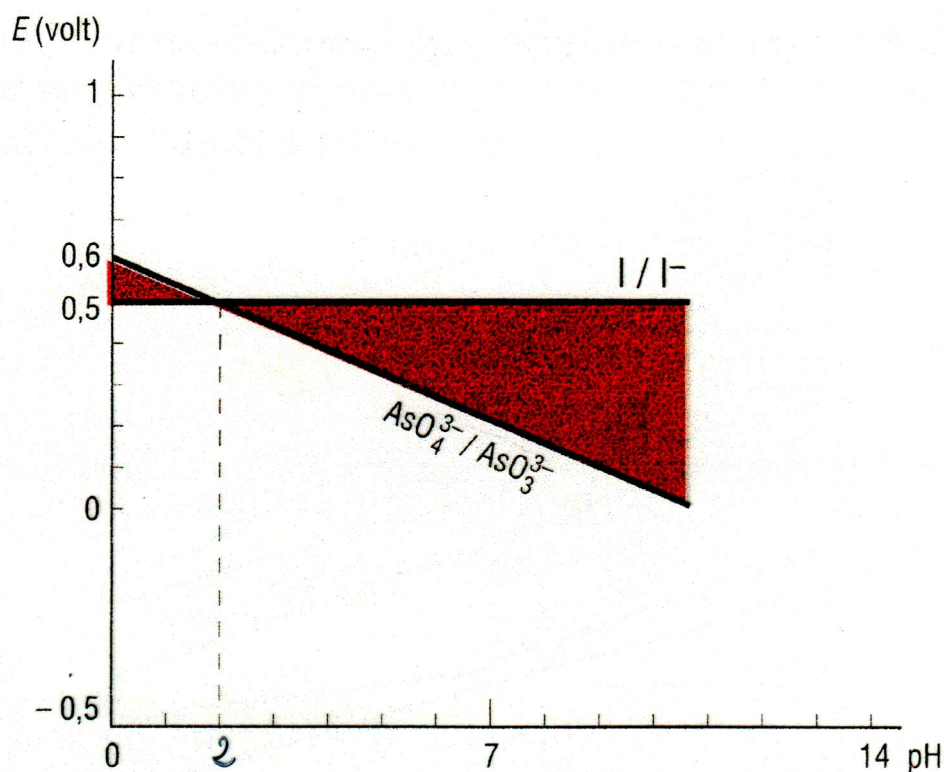
$$E = E^\circ + \frac{0.06}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{+3}]^2} + \frac{0.06}{6} \log [\text{H}^+]^{14}$$

$$E = E^\circ + \frac{0.06}{6} \log [\text{H}^+]^{14}$$

$$E = 1.30 - 0.14 \text{ pH}$$

pH = 0	E = 1.30 V	E = 1.75 V	0.45
pH = 3	E = 0.88 V	E = 1.39 V	0.51
pH = 5	E = 0.60 V	E = 1.15 V	0.55
pH = 7	E = 0.32 V	E = 0.91 V	0.59
pH = 10	E = -0.1 V	E = 0.55 V	0.65
	$\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{+3}$	$\text{PbO}_2 / \text{Pb}^{+2}$	$\Delta E$

# ESEMPIO II $\equiv$ ARSENITI E ARSENIATI CON $I_2$

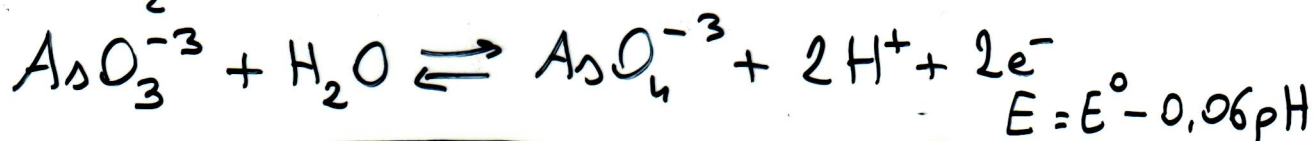
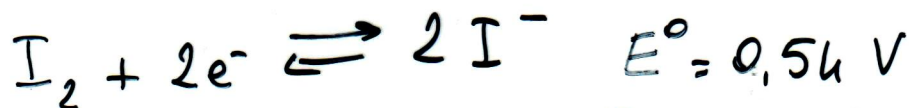


A  $pH < 2$  :



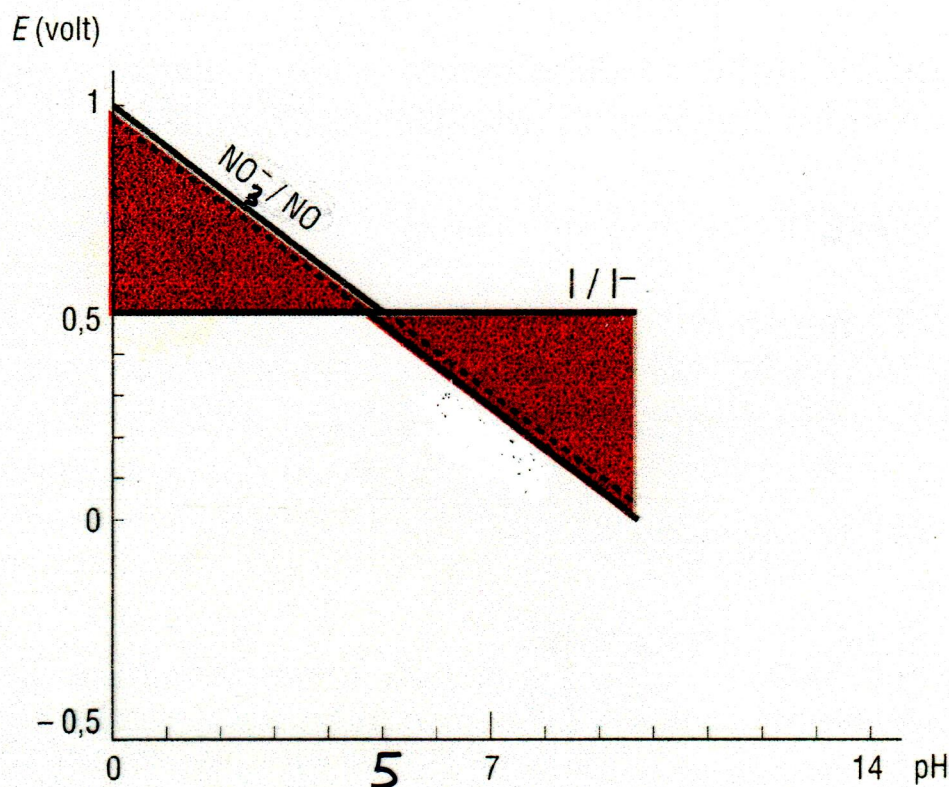
*viola* in  $CHCl_3$

A  $pH > 2$  :

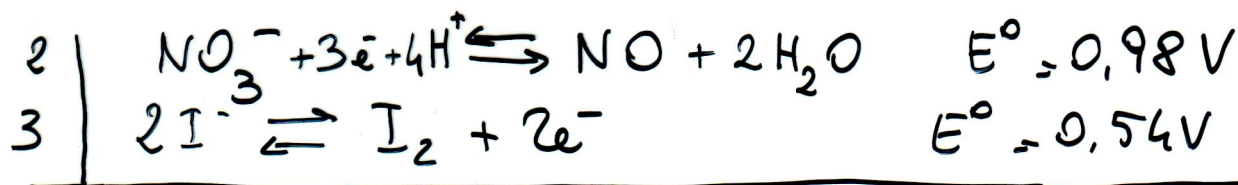




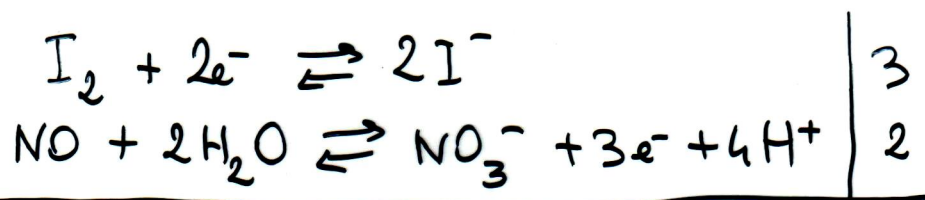
# ESEMPIO III $\equiv$ NITRATI E IODURI



A  $\text{pH} < 5$  si ha:

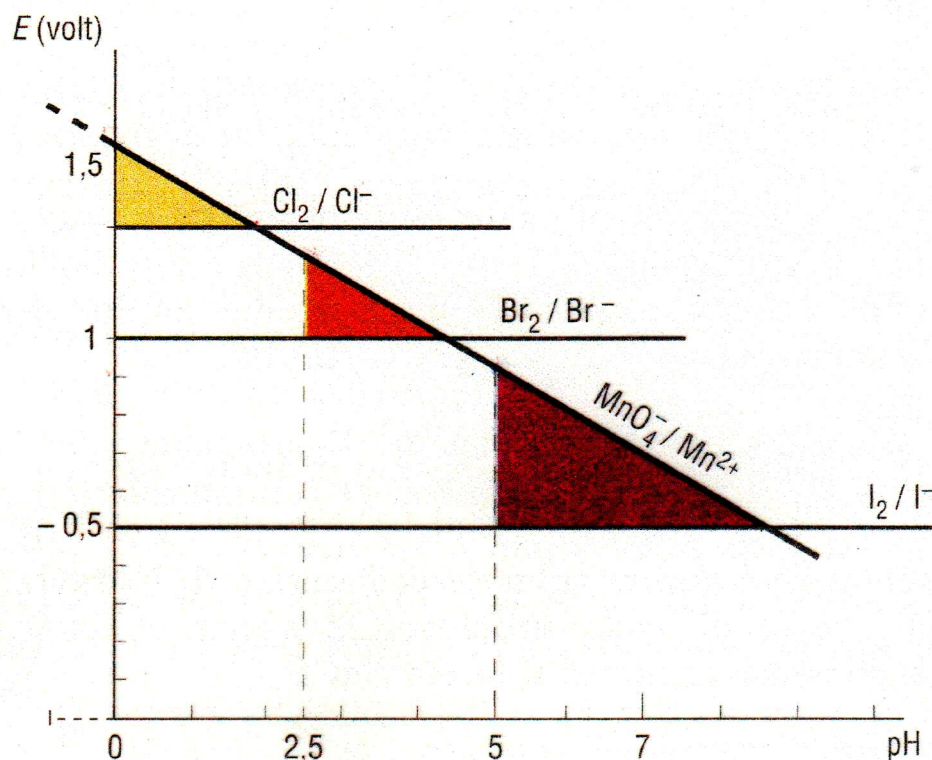


a  $\text{pH} > 5$ :

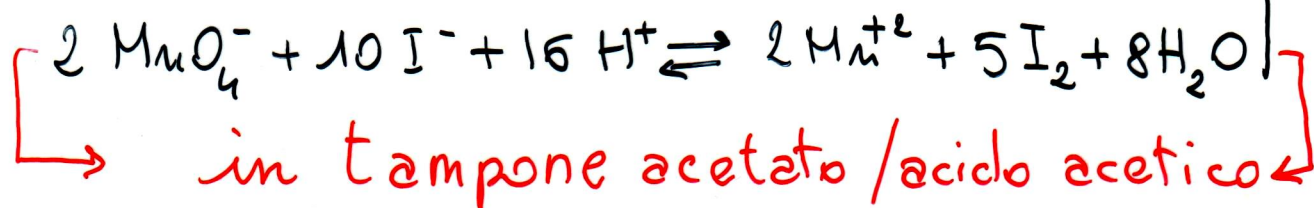
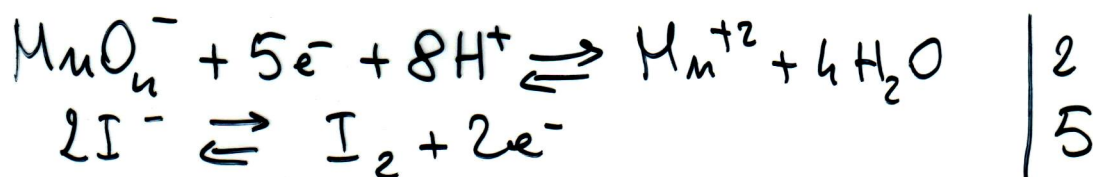


Per cui nella soluzione ALCALINA degli anioni, anche se presenti contemporaneamente  $\text{NO}_3^-$  e  $\text{I}^-$  non reagiscono.

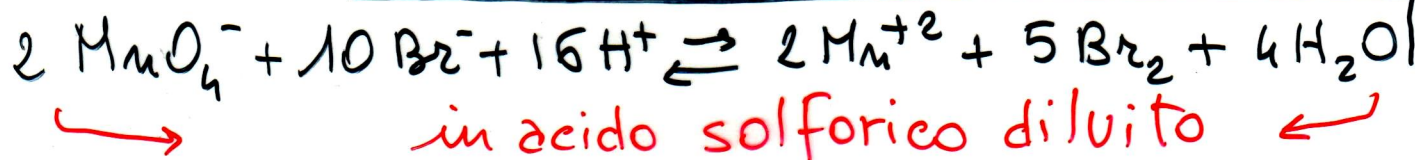
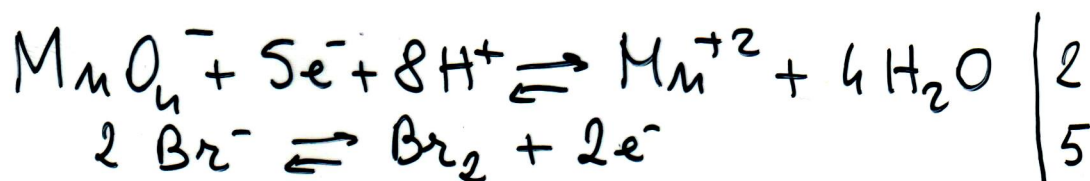
# ESEMPIO IV $\equiv$ OSSIDAZIONE SELETTIVA DEGLI ALOGENURI CON $\text{MnO}_4^-$



A  $\text{pH} = 5$  il  $\text{MnO}_4^-$  ossida solo gli  $\text{I}^-$  a  $\text{I}_2$ :

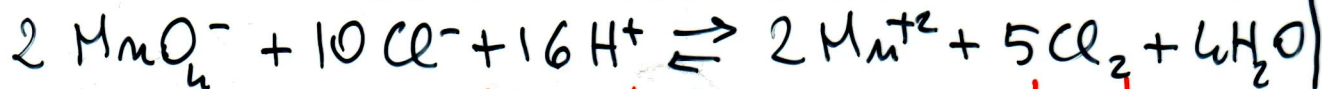
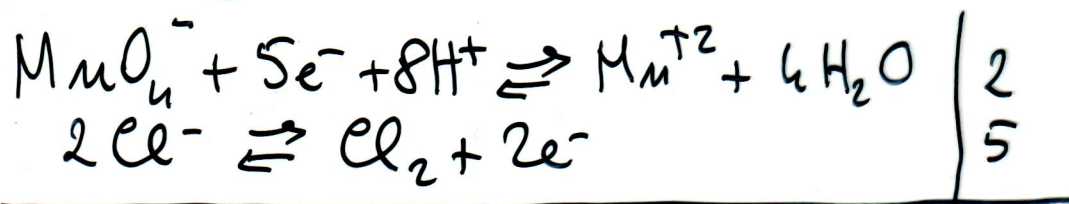


A  $\text{pH} = 2,5$ , eliminati gli  $\text{I}^-$ ,  $\text{MnO}_4^-$  ossida selettivamente:  $\text{Br}^-$  e  $\text{Br}_2$ :



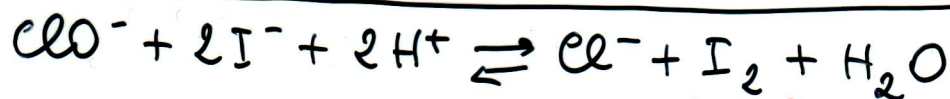
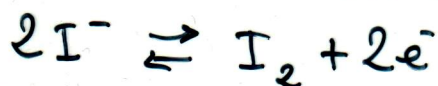
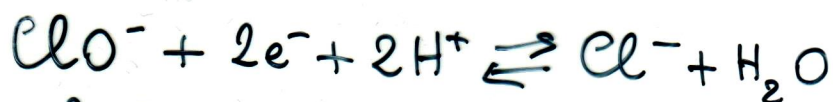
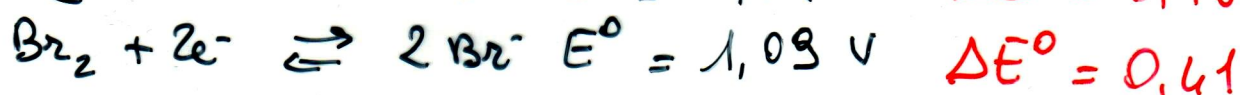
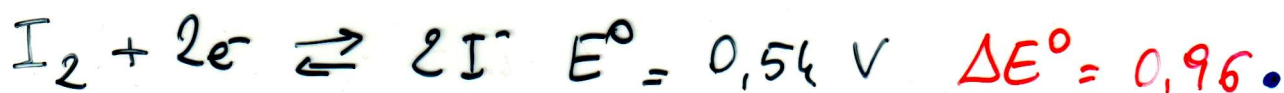


A  $\text{pH} = 0$ , assenti  $\text{I}^-$  e  $\text{Br}^-$  il  $\text{MnO}_4^-$  ossida  
i  $\text{Cl}^-$  a  $\text{Cl}_2$

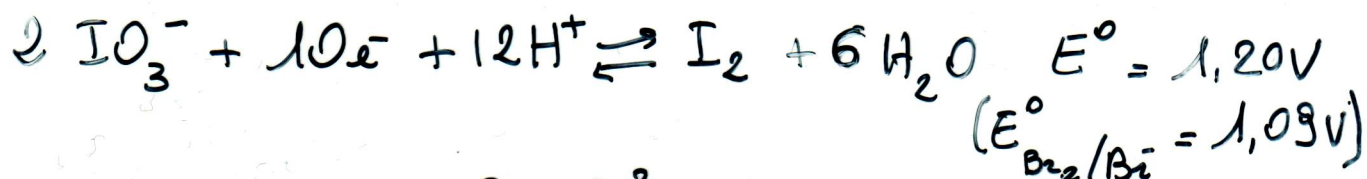


→ in acido nitrico concentrato ←

ESEMPIO V  $\equiv$  OSSIDAZIONE DI  $\text{I}^-$  E  $\text{Br}^-$   
CON IPOCLORITO ( $\text{ClO}^-$ )



viola in  $\text{CHCl}_3$



$$E = E^\circ + \frac{0,06}{10} \log \frac{[\text{IO}_3^-]^2}{[\text{I}_2]} + \frac{0,06}{10} \log [\text{H}^+]^{12}$$

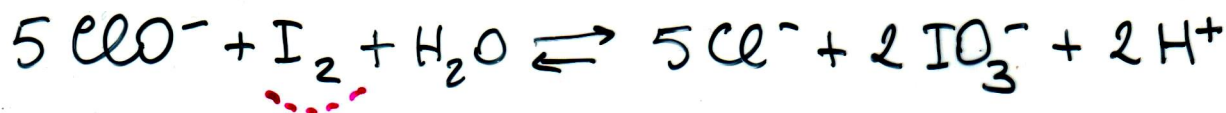
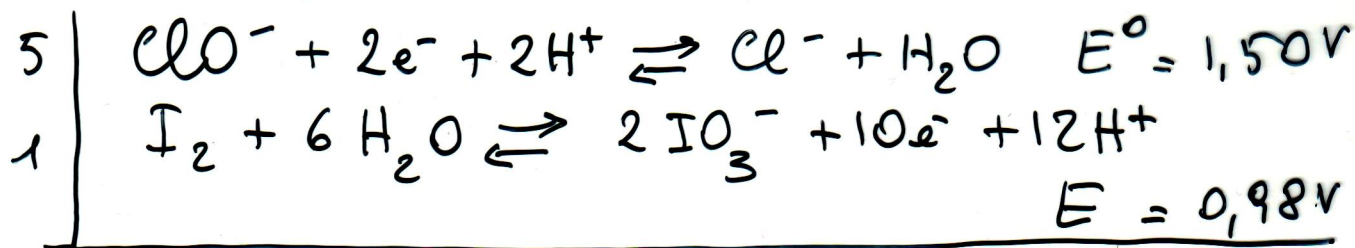
$$E = E^\circ - \frac{0,06 \cdot 12}{10} \text{pH} = 1,20 - 0,07 \text{pH}$$

a  $\text{pH} = 3$  :  $E = 1,20 - 0,21 = \underline{0,98\text{V}} < 1,09 \text{ } E^\circ_{\text{Br}_2/\text{Br}^-}$

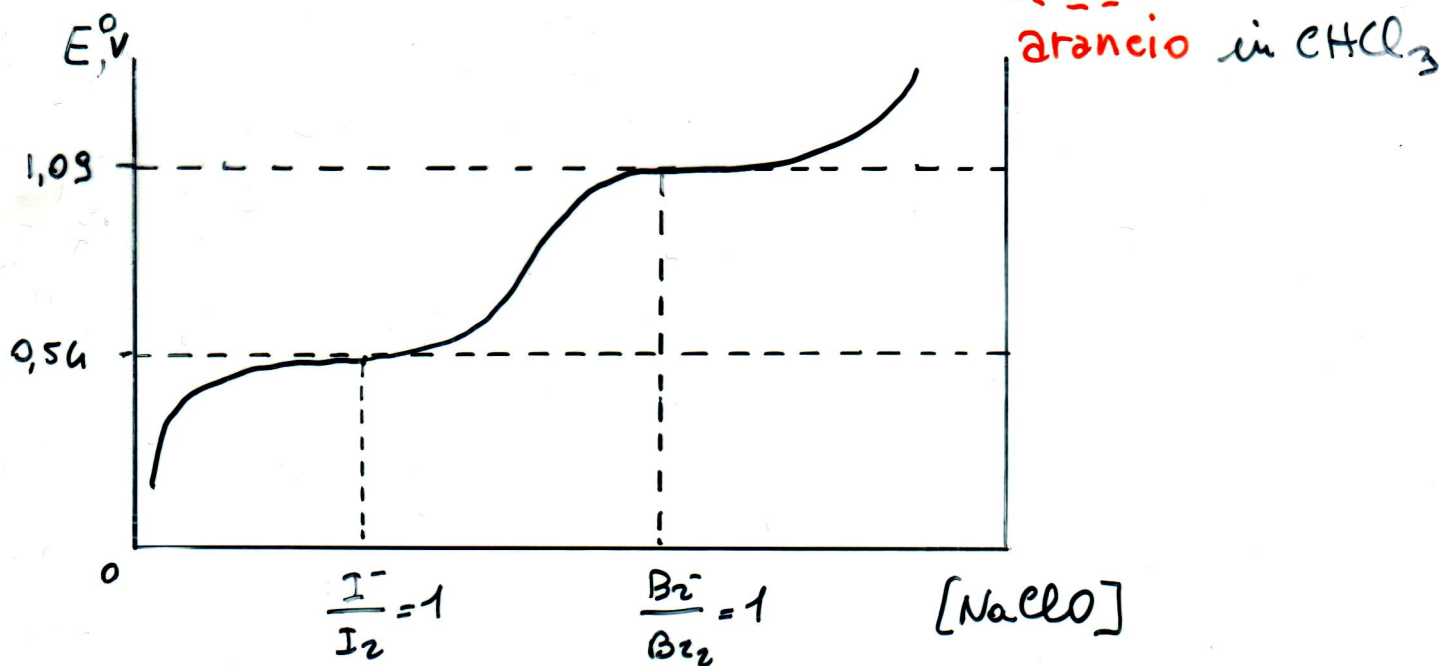
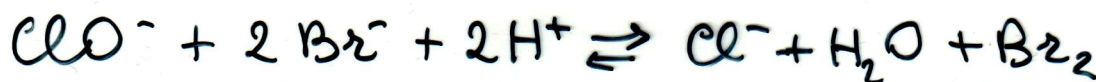
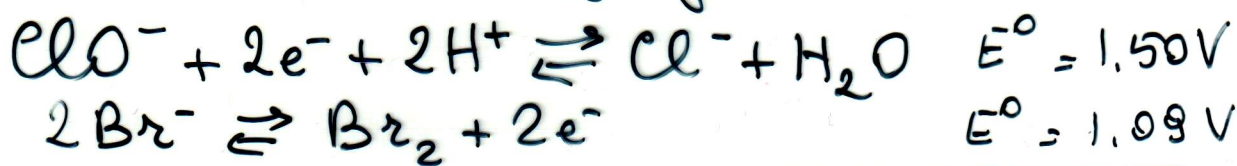
e a  $\text{pH} = 5$  :  $E_{\text{IO}_3^-/\text{I}_2} = 1,20 - 0,35 = \underline{0,85\text{V}}$



Quindi a  $\text{pH}=3$  si avrà:

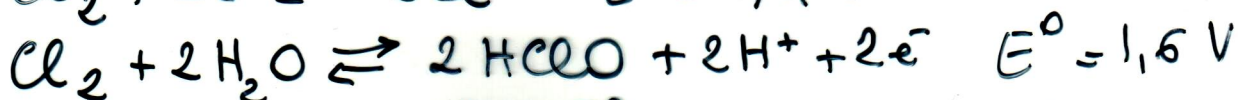


e continuando ad aggiungere ipoclorito:



## ESEMPIO VI $\equiv$ REAZIONI DI DISPROPORZIONE

Il CLORO, a  $\text{pH} > 3,3$  subisce una reatt. di disproporz.



$$E_{\text{red-ox}} = E^\circ + \frac{0,06}{n} \log \frac{[\text{HClO}]^2}{[\text{Cl}_2]} + \frac{0,06}{n} \log [\text{H}^+]^2$$

$$E = E^{\circ} - 0,06 \text{ pH} = 1,6 - 0,06 \text{ pH}$$

A  $\text{pH} = 3,3$   $E_{\text{ClO}^-/\text{Cl}_2} = 1,4 \equiv E^{\circ}_{\text{Cl}_2/\text{Cl}^-}$  = PUNTO TRIPLO  
coesistenza  $\text{HClO}$ ,  $\text{Cl}^-$ ,  $\text{Cl}_2$

$\text{pH} < 3,3$  :  $\text{HClO}$  reagisce con  $\text{Cl}^-$  per dare  $\text{Cl}_2$

$\text{pH} > 3,3$  :  $\text{Cl}_2$  non è stabile e disproporziona in  $\text{HClO}$  e  $\text{Cl}^-$

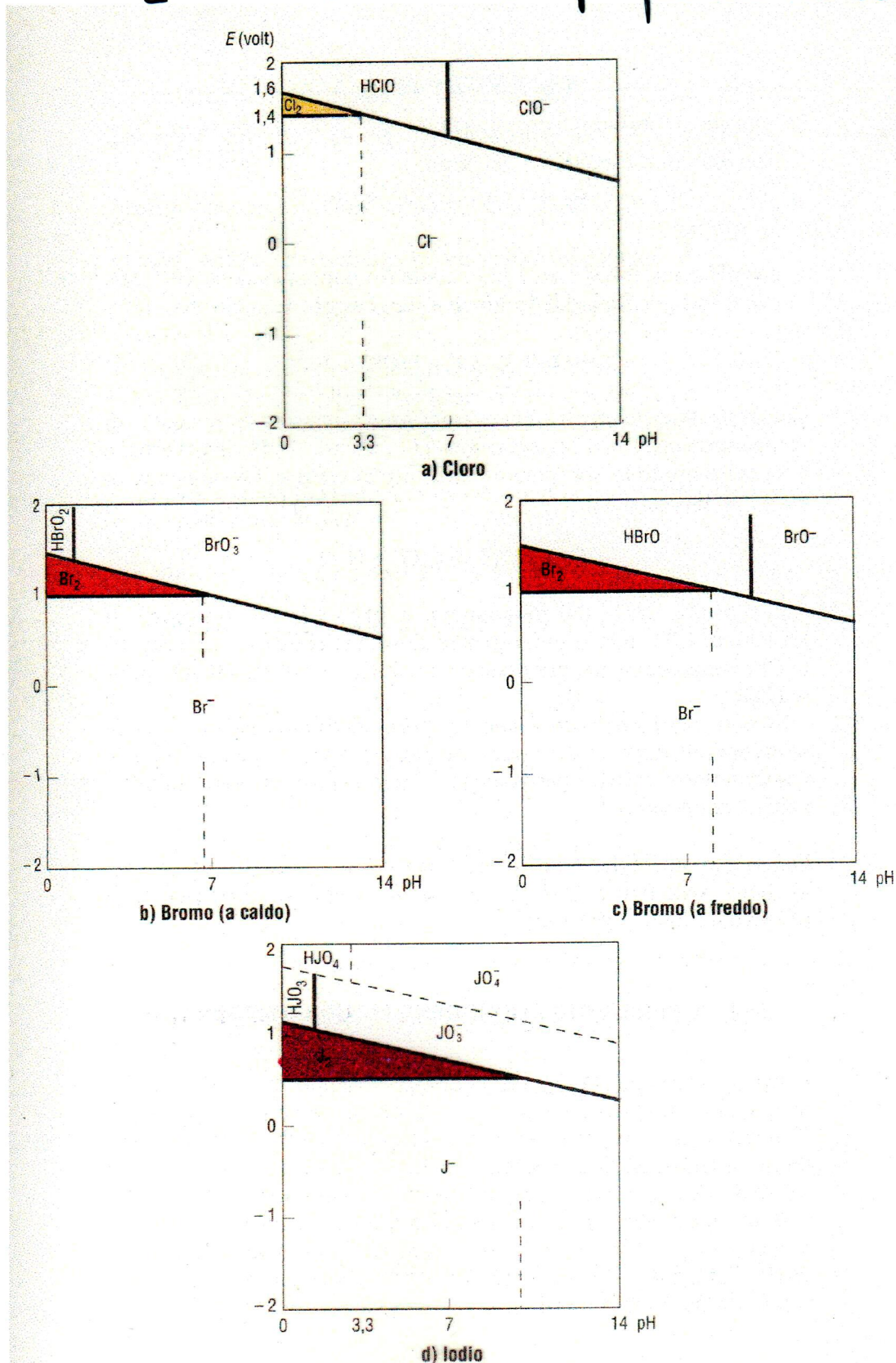


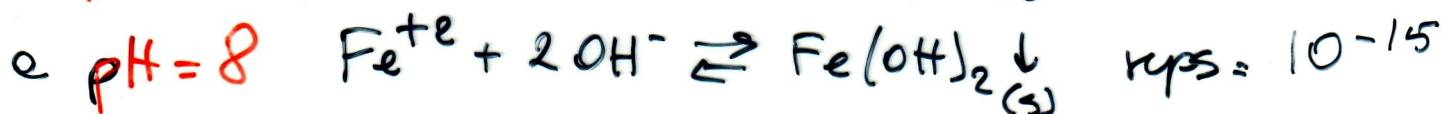
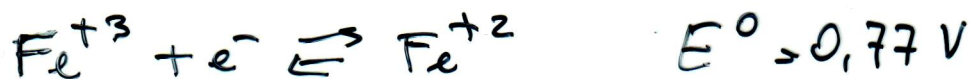
FIGURA 11-3-1 Sproporzionamento degli alogeni.



# 6. INFLUENZA DEGLI EQUILIBRI DI PRECIPITAZIONE SUGLI EQUILIBRI REDOX

(No)

ESEMPIO I  $\equiv$  COPPIA  $Fe^{+3}/Fe^{+2}$



$$E = E^0 + 0,06 \log \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

$$E = E^0 + 0,06 \log \frac{10^{-38} [OH^-]^3}{[OH^-]^3 \cdot 10^{-15}} = E^0 + 0,06 \log \frac{10^{-23}}{[OH^-]}$$

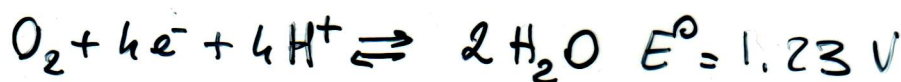
$$E = E^0 - 1,38 + \log \frac{1}{[OH^-]} = 0,77 - 1,38 + 0,06 pOH$$

$$E = -0,6 + 0,06 pOH$$

Un sale di  $Fe^{+2}$  si ossiderà allora all'aria più facilmente in ambiente alcalino:

$pH=0$

$$E_{Fe^{+3}/Fe^{+2}} = E^0 = 0,77 V$$



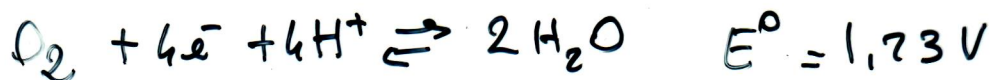
$$E = E^0 + \frac{0,06}{4} \log \frac{[O_2][H^+]^4}{[H_2O]^2}$$

$$E = E^0 + \frac{0,06}{4} \log [H^+]^4$$

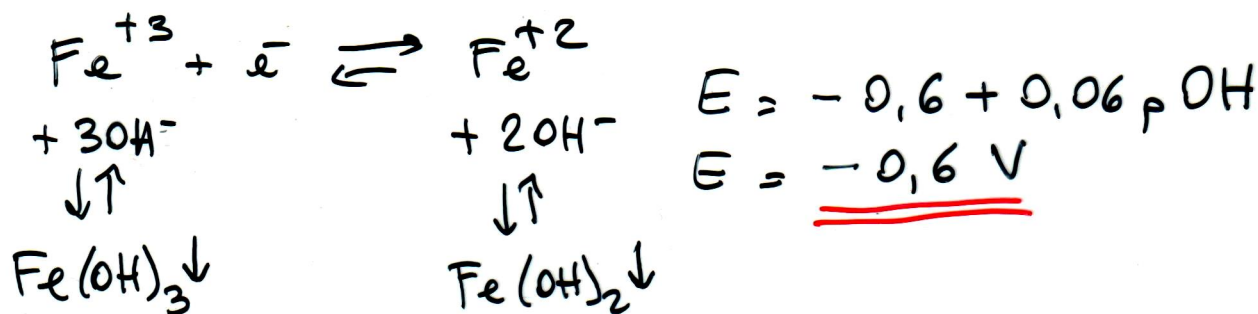
$$E = E^0 - 0,06 pH$$

$$\Delta E = 0,46$$

$$pH = 14$$



$$E = E^0 - 0,06 pH = 1,73 - 0,84 = \underline{\underline{0,39V}}$$



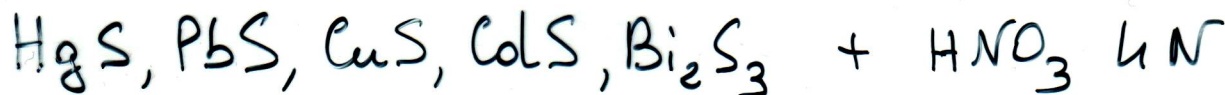
$$\Delta E = 0,39 - (-0,6) = \underline{\underline{0,99}} \gg 0,46$$

ESEMPIO II  $\equiv$  OSSIDAZIONE DI SOLFURI  
POCO SOLUBILI CON  $HNO_3$

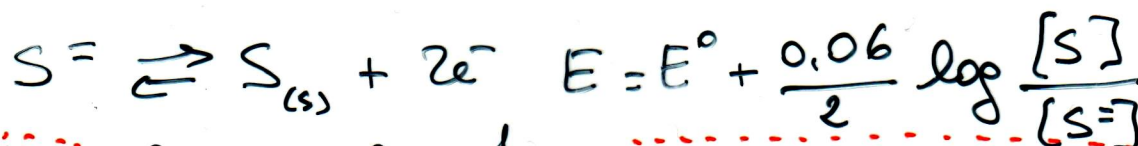
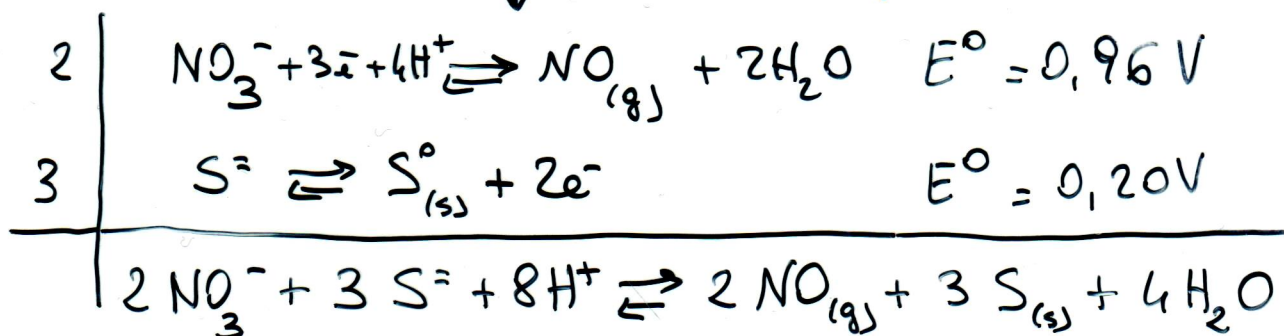
2° GRUPPO ANALITICO RICERCA CATIONI

1° SOTTOGRUPPO: solfuri basici:

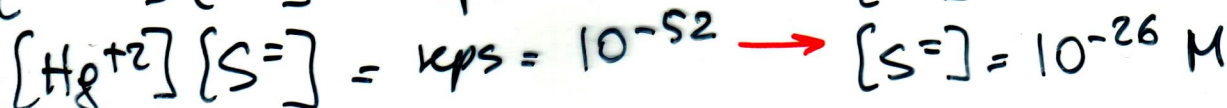
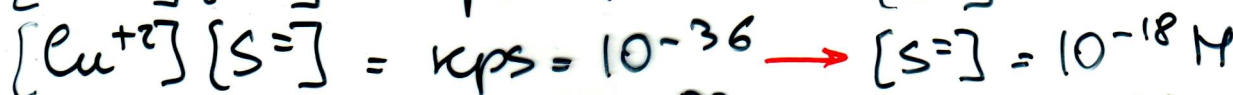
(SI)



↓ tutti tranne  $HgS$



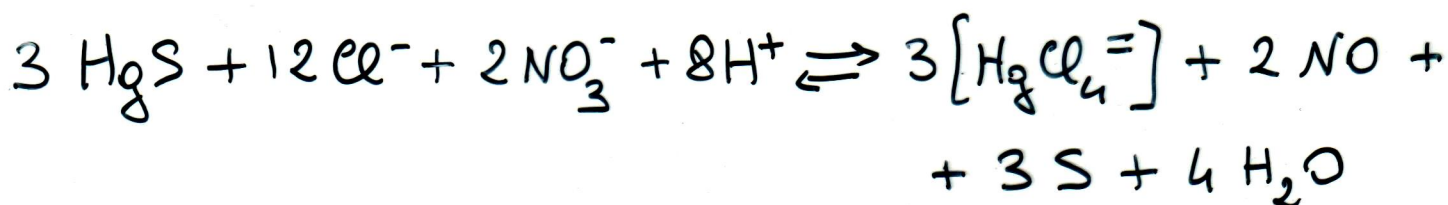
$$(E = E^0 + 0,03 \log \frac{1}{[S^=]} = 0,2 + 0,03 p[S^=])$$



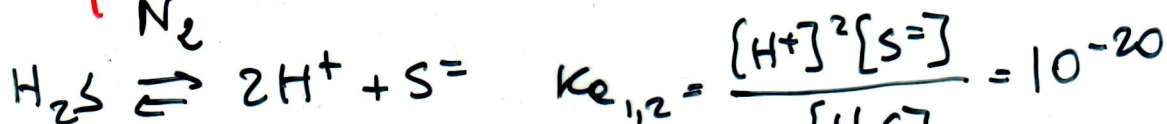
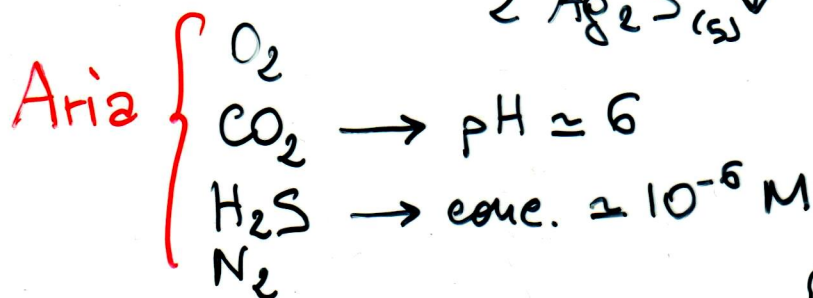
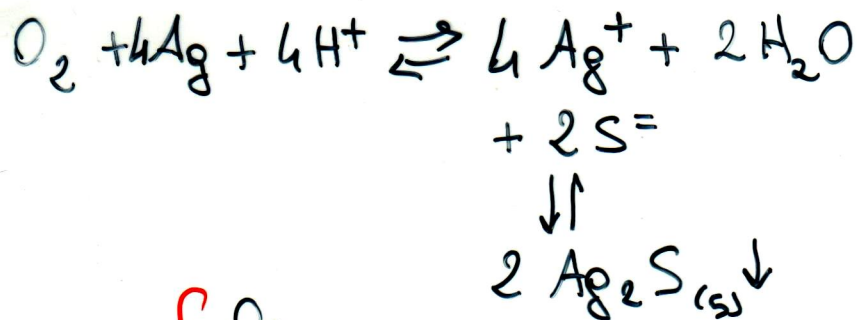
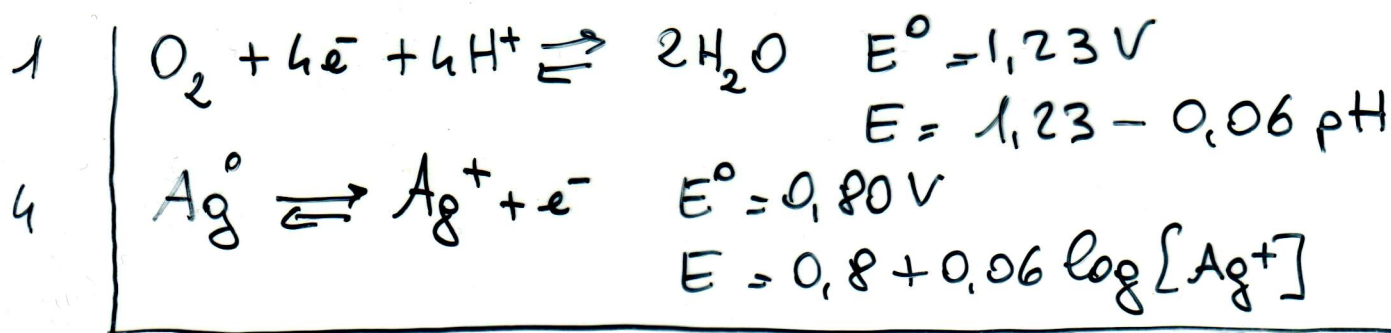


$$E^{\circ}_{\text{NO}_3^-/\text{NO}} = 0,96 \text{ V}$$

$$E_{\text{S}/\text{S}^{2-}} = 0,2 + 0,03 \text{ p}[\text{S}^{2-}] \begin{cases} \text{PbS} : E_{\text{S}/\text{S}^{2-}} = 0,62 \text{ V} \\ \text{CuS} : E_{\text{S}/\text{S}^{2-}} = 0,74 \text{ V} \\ \text{HgS} : E_{\text{S}/\text{S}^{2-}} = \underline{\underline{0,98 \text{ V}}} \end{cases}$$



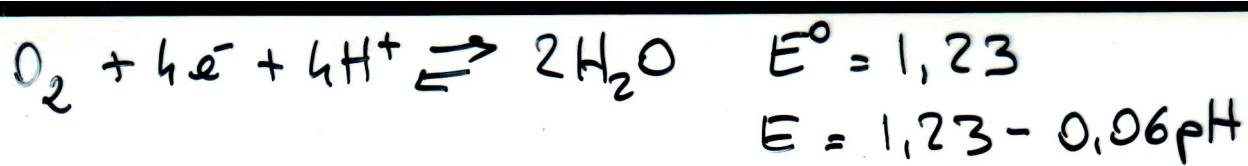
### ESEMPIO 3 $\equiv$ OSSIDAZIONE DELL' ARGENTO METALLICO ALL' ARIA



$$[\text{S}^{2-}] = \frac{K_{e,1,2} [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{10^{-20} \cdot 10^{-6}}{(10^{-6})^2} = \underline{\underline{10^{-14} \text{ M}}} \quad \begin{array}{l} \text{concentrat.} \\ \text{S}^{2-} \text{ nell' } \\ \text{aria} \end{array}$$

$$K_{ps, \text{Ag}_2\text{S}} = [\text{Ag}^+]^2 [\text{S}^{2-}] = 10^{-50}$$

$$[\text{Ag}^+] = \sqrt{\frac{10^{-50}}{10^{-14}}} = \sqrt{\frac{10^{-50}}{10^{-14}}} = 10^{-18} \text{ M}$$



a pH = 6:

$$E = 0,87 V \text{ nell'aria}$$



$$E = 0,8 + 0,06 \log [Ag^+]$$

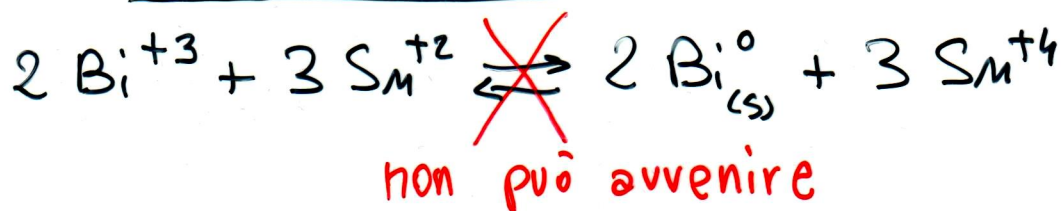
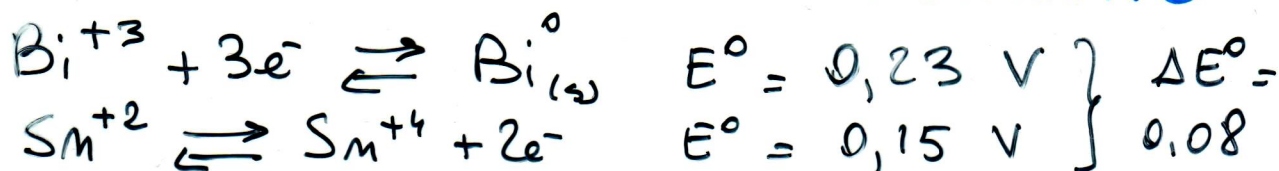
$$E = 0,8 + 0,06 \log 10^{-18}$$

$$E = 0,8 - 1,08 = -0,28 V$$

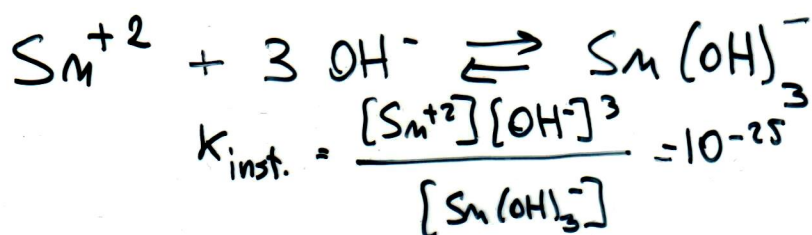
nell'aria in presenza  
di  $S^{2-}$

## 7. INFLUENZA DELLA FORMAZIONE DI COMPLESSI SUGLI EQUILIBRI REDOX

ESEMPIO I  $\equiv$  RIDUZIONE DEL  $Bi^{+3}$  a  $Bi^0$   
CON IDROSSISTANNITO ALCALINO

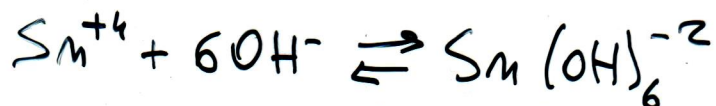


A pH = 14:

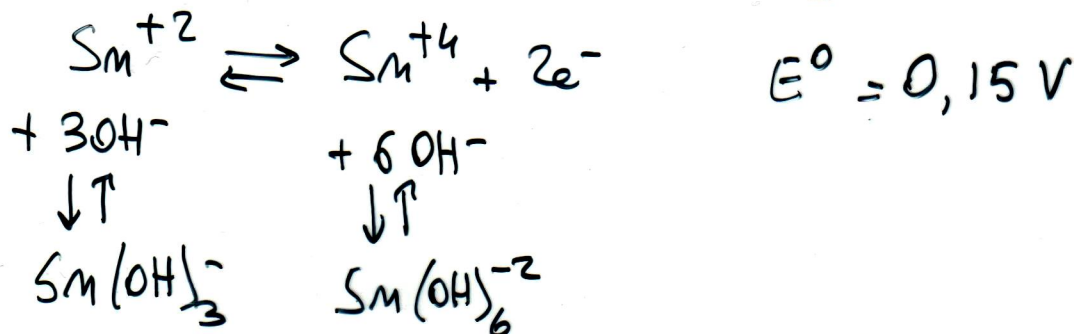




$$pH = 14$$



$$K_{inst} = \frac{[Sn^{+4}][OH^-]^6}{[Sn(OH)_6^{-2}]} = 10^{-63}$$



$$E = E^0 + \frac{0,06}{2} \log \frac{[Sn^{+4}]}{[Sn^{+2}]}$$

$$E = E^0 + 0,03 \log \frac{10^{-63} \cdot [Sn(OH)_6^{-2}]}{[OH^-]^6} \cdot \frac{[OH^-]^3}{10^{-25} \cdot [Sn(OH)_3^-]}$$

$$E = E^0 + 0,03 \log \frac{10^{-38} \cdot [Sn(OH)_6^{-2}]}{[OH^-]^3 \cdot [Sn(OH)_3^-]}$$

$$E = 0,15 - 1,14 + 0,03 \log \frac{[Sn(OH)_6^{-2}]}{[Sn(OH)_3^-]} + 0,03 \log \frac{1}{[OH^-]^3}$$

$$E = -0,99 + 0,03 \log \frac{[Sn(OH)_6^{-2}]}{[Sn(OH)_3^-]} + 0,09 pOH$$

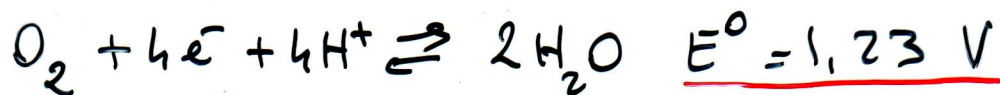
$$E = -0,99 + 0,09 pOH$$

$$\text{at } pH = 14 \quad pOH = 0$$

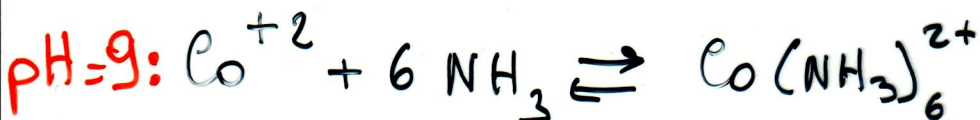
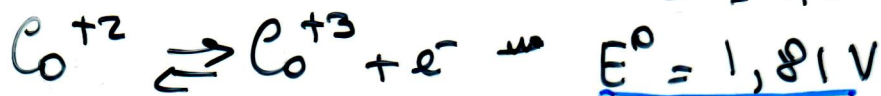
$$E_{Sn^{+4}/Sn^{+2}} = -0,99 V$$

$$E_{Bi^{+3}/Bi} = +0,23 V$$

# ESEMPIO II $\equiv$ OSSIDAZIONE DEL $\text{Co}^{+2}$ A $\text{Co}^{+3}$ ALL' ARIA

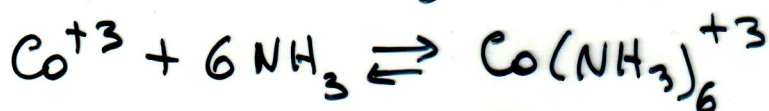


$$E = 1,23 - 0,06 \text{ pH}$$



$\text{NH}_3 \text{ 1M}$

$$K_{\text{inst}} = \frac{[\text{Co}^{+2}][\text{NH}_3]^6}{[\text{Co}(\text{NH}_3)_6^{+2}]} = 10^{-6}$$



$$K_{\text{inst}} = \frac{[\text{Co}^{+3}][\text{NH}_3]^6}{[\text{Co}(\text{NH}_3)_6^{+3}]} = 10^{-38}$$

$$E = E^\circ + 0,06 \log \frac{[\text{Co}^{+3}]}{[\text{Co}^{+2}]}$$

$$E = E^\circ + 0,06 \log \frac{10^{-38} \cdot [\text{Co}(\text{NH}_3)_6^{+3}] \cdot [\text{NH}_3]^6}{10^{-6} \cdot [\text{Co}(\text{NH}_3)_6^{+2}] \cdot [\text{NH}_3]^6}$$

$$E = E^\circ + 0,06 \log \frac{10^{-32} \cdot [\text{Co}(\text{NH}_3)_6^{+3}]}{[\text{Co}(\text{NH}_3)_6^{+2}]}$$

$$E = E^\circ - 1,92 + 0,06 \log \frac{[\text{Co}(\text{NH}_3)_6^{+3}]}{[\text{Co}(\text{NH}_3)_6^{+2}]}$$

$$E_{\text{Co}^{+3}/\text{Co}^{+2}} = 1,81 - 1,92 = -0,11 \text{ V} \quad \text{a } \text{pH} = 9; \text{NH}_3 = 1\text{M}$$

$$E_{\text{O}_2/\text{H}_2\text{O}} = 1,23 - 0,06 \text{ pH} = 0,69 \text{ V} \quad \text{a } \text{pH} = 9$$