$$Cd^{2+} + Fe \rightleftharpoons Cd + Fe^{2+}$$

$$Cd^{2+} + 2e^- \rightleftharpoons Cd$$

$$Fe \rightleftharpoons Fe^{2+} + 2e^-$$

$$Cd^{2+} + Fe \rightleftharpoons Cd + Fe^{2+}$$

$$2Fe_{(s)} + 3Cl_2 \rightleftharpoons 2Fe^{3+} + 6Cl^-$$

$$2 \times (2Fe^0 \longrightarrow 2Fe^{3+} + 6e^-) \quad \text{ossi.}$$

$$3 \times (3Cl_2 + 2e^- \longrightarrow 2Cl^-) \quad \text{rid.}$$

$$14H_2O + 4FeS_2 + 15O_2 \rightleftharpoons 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+$$

$$15 \left[O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \right]$$

$$4 \left[FeS_2 + 11H_2O \longrightarrow Fe(OH)_3 + 19H^+ + 2SO_4^{2-} + 15e^- \right]$$

$$pH = -\log [H^+]$$

$$pE = -\log \{e^-\}$$

→ ATTIVITÀ ELETTRONICA

Acido - base

$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_1$

$HA \rightleftharpoons H^+ + A^- \quad K_2$

$H^+ + H_2O \rightleftharpoons H_3O^+ \quad K_3$

$\Delta\zeta^\circ = 0 \qquad K_3 = 1$

$K_1 = K_2 \cdot K_3 = K_2$

$$K_1 = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \{H^+\}$$

$$[H^+] = K_1 \cdot \frac{[HA]}{[A^-]}$$

$$\log [H^+] = \log K_1 + \log \frac{[HA]}{[A^-]}$$

RED - OX

$Fe^{3+} + \frac{1}{2} H_{2(g)} \rightarrow Fe^{2+} + H^+ \quad K_1$

$\frac{1}{K_2} H_2 \rightleftharpoons H^+ + e^- \quad K_3$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad K_2$

$\Delta\zeta^\circ = 0 \qquad K_3 = 1$

$K_1 = K_2 \cdot K_3 = K_2 = \frac{[Fe^{2+}]}{[Fe^{3+}][e^-]}$

$$[e^-] = \frac{[Fe^{2+}]}{[Fe^{3+}] \cdot K_1}$$

$\{e^-\} \leftrightarrow [e^-]$

$$-\log \{e^-\} = -\log \frac{1}{K_1} - \log \frac{[E^{2+}]}{[Fe^{3+}]}$$

$$-\log[H^+] = -\log K_1 - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_1 + \log\frac{[A^-]}{[HA]}$$

$$-\log[e^-] = -\log\frac{1}{K_1} - \log\frac{[E^{2+}]}{[Fe^{3+}]}$$

$$-\log[e^-] = \log K_1 + \log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE = pE^\circ + \log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE^\circ = \log K_1$$

$$Ox + \left(\frac{u}{2}\right) H_2 \rightleftharpoons Red + u H^+$$

$$pE = pE^\circ + \frac{1}{u}\log\frac{[Ox]}{[Red]}$$

$$pE^\circ = \frac{1}{u}\log K$$

$$pE = pE^\circ + \frac{1}{u}\log\frac{\prod [Ox]^{n_i}}{\prod [Red]^{m_j}}$$

$$pE^\circ = \frac{1}{n}\log K$$

① pE?

Fe^{3+} 10^{-5} M e Fe^{2+} 10^{-3} M

$pE^0 = \log K = 13$

$$pE = pE^0 + \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$\rightarrow 13 + \log \frac{10^{-5}}{10^{-3}} = 11$$

---

pE? pH 7.5

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

$$\log K = 41.55$$

$$pE = pE_0 + \frac{1}{2} \log \left(P_{O_2}^{1/2} \cdot [H^+]^2 \right)$$

$$= 20.78 + \frac{1}{2} \log \left[0,2 \cdot (10^{-7.5})^2 \right]$$

$$= 13.43$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

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

$$Fe_T = [Fe^{2+}] + [Fe^{3+}] \qquad Fe_T - [Fe^{3+}] = [Fe^{2+}]$$

$$K = \frac{Fe_T - [Fe^{3+}]}{[Fe^{3+}][e^-]}$$

$$K([Fe^{3+}] \cdot [e^-]) = Fe_T - [Fe^{3+}]$$

$$Fe_T = K([Fe^{3+}] \cdot [e^-]) + [Fe^{3+}]$$

$$\overset{!}{=} [Fe^{3+}](K \cdot [e^-] + 1)$$

$$[Fe^{3+}] = \frac{Fe_T}{K \cdot [e^-] + 1}$$ dividi K

$$\overset{|}{=} \frac{Fe_T / K}{[e^-] + \frac{1}{K}} = \frac{Fe_T \cdot K^{-1}}{(e^-) + K^{-1}}$$

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

$$[Fe^{3+}] = Fe_T - [Fe^{2+}]$$

$$Fe_T = [Fe^{2+}] + [Fe^{3+}]$$

$$K = \frac{[Fe^{2+}]}{(Fe_T - [Fe^{2+}])\,[e^-]}$$

$$K \cdot [e^-] \cdot (Fe_T - [Fe^{2+}]) = [Fe^{2+}]$$

$$K \cdot [e^-] \cdot Fe_T - K \cdot [e^-] \cdot [Fe^{2+}] = [Fe^{2+}]$$

$$[Fe^{2+}](1 + K \cdot [e^-]) = K[e^-] \cdot Fe_T$$

$$[Fe^{2+}] = \frac{K \cdot [e^-] \cdot Fe_T}{1 + K \cdot [e^-]}$$ durch K

$$= \frac{K[e^-] \cdot Fe_T / K}{\frac{1 + K[e^-]}{K}}$$

$$[Fe^{2+}] = \frac{[e^-] \cdot F_T}{\frac{1}{K} + [e^-]} = \frac{Fe_T \cdot [e^-]}{[e^-] + K^{-1}}$$

$$p\mathcal{E} = p\mathcal{E}^\circ + \varphi \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$p\mathcal{E}^\circ = \varphi K_1$$

$$\varphi C - p\mathcal{E}$$

$$[Fe^{2+}] = \frac{Fe_T \cdot [e^-]}{(e^-) + K^{-1}} \qquad [Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{[e^-] + K^{-1}}$$

$$[e^-] \gg K^{-1} \qquad [Fe^{2+}] = \frac{Fe_T \cdot \cancel{[e^-]}}{\cancel{[e^-]}} \simeq Fe_T$$

$$p\mathcal{E} = p\mathcal{E}^\circ + \varphi \frac{[Fe^{3+}]}{Fe_T}$$

$$\varphi[Fe^{3+}] = \varphi Fe_T + p\mathcal{E} - p\mathcal{E}^\circ$$

$$\varphi[Fe^{2+}] \simeq \varphi Fe_T$$

$[e^-] \ll K^{-1}$

$$[Fe^{2+}] = \frac{Fe_T \cdot [e^-]}{[e^-] + K^{-1}} \qquad [Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{[e^-] + K^{-1}}$$

$$[Fe^{3+}] = \frac{Fe_T \cdot K^{-1}}{K^{-1}} \simeq Fe_T$$

$$\log [Fe^{3+}] \simeq \log Fe_T$$

$$pE = pE^\circ + \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$pE = pE^\circ + \log \frac{Fe_T}{[Fe^{2+}]}$$

$$\log [Fe^{2+}] = \log Fe_T + pE^\circ - pE$$

$2H^+$

$\log K = -28 \quad 2H_2O + 4H^+ + 2e^- \longrightarrow 3H_{2(g)} + 2OH^-$

$\log K = 0 \quad 2H^+ + 2e^- \rightleftharpoons H_{2(g)}$

$\log K = 83.1 \quad O_{2(g)} + 4H^+ + 4e \rightleftharpoons 2H_2O$

$\log K = 27.1 \quad O_{2(g)} + 2H_2O + 8e^- \rightleftharpoons 4OH^-$

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

$$\Delta G = -50{,}8 \text{ kcal/mole}$$

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

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

ΔE $\quad$ ΔG°

$$E^\circ_{Cu/Cu^{2+}} = +0{,}34 \text{ V}$$

$$E^\circ_{Zn/Zn^{2+}} = -0{,}76 \text{ V}$$

ΔG° $\quad$ ΔE°

ΔG° $\quad$ (K)

$$\Delta E = \frac{W_u}{nF}$$

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

$$W_u = -\Delta G_r$$

$$\Delta E = -\frac{\Delta G}{nF}$$

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

$$K = \frac{[Zn^{2+}]}{[Zn]} \qquad n = 2$$

$$E = E^\circ_{H} + \frac{2{,}3025\,RT}{2F} \lg [Zn^{2+}]$$

$25^\circ C$

$$= E^\circ_{H} + \frac{0{,}0592}{2} \lg [Zn^{2+}]$$

$$E = E^\circ_{H} + 0{,}0296 \lg [Zn^{2+}]$$

$$Zn + 2H^+ \rightleftharpoons Zn^{2+} + H_2(g)$$

25° $\quad n=2$

$$E = E^\circ + \frac{0{,}0592}{2} \log \frac{[Zn^{2+}]\, pH_2}{[H^+]^2 \cdot 1}$$

$1 \quad 1$

$$= E^\circ + \frac{0{,}0592}{2} \log [Zn^{2+}]$$

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -RT \ln K_1$$

$$pE^\circ = \frac{1}{n} \log K_1$$

$$\log K_1 = -\frac{\Delta G^\circ}{RT\, 2{,}3}$$

$$= \frac{1}{n} \cdot \frac{-\Delta G^\circ}{2{,}3RT} = \frac{1}{n} \cdot \frac{nF}{2{,}3RT} E_H^\circ$$

$$pE^\circ = \frac{F}{2{,}3RT} E_H^\circ$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

$$pE = pE^\circ + \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

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

$pE - pH$ $\quad H_2O$

$$\frac{1}{2} O_{2(g)} + 2H^+ + 2e^- \rightleftharpoons H_2O_{(l)}$$

$$E^\circ_H = 1{,}23\ V$$

$$E_H = E^\circ_H + 0{,}0295 \log \frac{p O_2^{1/2} \cdot [H^+]^2}{}$$

$$E = 1{,}23 + 0{,}0147 \log p O_2 - 0{,}059\, pH$$

(1)

$$E = 1{,}23 - 0{,}059\, pH$$

$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2(g)$

$E_H = E^0 + 0{,}059 \log\left(\frac{[H^+]}{p H_2^{1/2}}\right)$

↑ 1 atm

$$E = -0{,}059\, pH$$

E_H - pH Cl_2 - Cl^- - ClO^-

$C_T = 10^{-4}$ M

① $HClO + H^+ + e^- \rightarrow \frac{1}{2} Cl_2 + H_2O$ $E^\circ_H = 1{,}59$ V

② $\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$ $E^\circ_H = 1{,}4$ V

③ $HClO \rightleftharpoons H^+ + ClO^-$ $pK_a = 7{,}3$

$C_T = 10^{-4}_M = 2[Cl_2] + [HClO] + [ClO^-] + [Cl^-]$

Courbe $HClO/Cl_2$

$HClO + H^+ + e^- \rightleftharpoons \frac{1}{2} Cl_2 + H_2O$ $E^\circ_H = 1{,}59$ V

$E = E^\circ_H - \frac{0{,}059}{1} \log \frac{[Cl_2]^{1/2}}{[H^+][HClO]}$

Il courbe $[Cl_2] = [HClO]$

$$E = E^\circ_H - \frac{0,0592}{1} \log \frac{[Cl_2]^{1/2}}{[H^+]\,[HClO]}$$

si on a $[Cl_2] = [HClO]$

$$2[Cl_2] + [HClO] \gg [ClO^-] + [Cl^-]$$

$$2[Cl_2] + [HClO] = 10^{-4}\ M = Cl_T$$

$$3[Cl_2] = 10^{-4}\ M$$

$$[Cl_2] = 3,3 \cdot 10^{-5}\ M.$$

$$[HClO] = Cl_T - 2[Cl_2] = 10^{-4} - 2(3,3 \cdot 10^{-5})$$

$$= 3,3 \cdot 10^{-5}$$

$$E = 1,59 - \frac{0,0592}{1} \log \frac{(3,3 \cdot 10^{-5})^{1/2}}{[H^+] \cdot 3,3 \cdot 10^{-5}}$$

$$= 1,59 - 0,0592 \log \frac{174}{[H^+]}$$

$$E = 1,46 - 0,0592\ pH$$

Coppia Cl_2/Cl^-

$$\frac{1}{2} Cl_2 + e^- \rightarrow Cl^- \qquad E^\circ = 1.4\ V$$

$$E = E^\circ - \frac{0,0592}{1} \log \frac{[Cl^-]}{[Cl_2]^{\frac{1}{2}}}$$

$$= 1,4 - 0,0592 \log \frac{(3.3 \cdot 10^{-5})}{(3.3 \cdot 10^{-5})^{\frac{1}{2}}}$$

$[Cl^-] = C(Cl_2)$ def. Coppia

$2[Cl_2] + [Cl^-] >> [HClO] + [ClO^-]$

$2[Cl_2] + [Cl^-] = 10^{-4}\ M = C_T$

$3[Cl_2] = 10^{-4} \Rightarrow [Cl_2] = 3.3 \cdot 10^{-5}\ M$

$[Cl^-] = C_T - 2[Cl_2]$

$= 10^{-4} - 2(3.3 \cdot 10^{-5}) = 3.3 \cdot 10^{-5}\ M$

$$E = E^\circ - \frac{0,0592}{1} \log \frac{[Cl^-]}{[Cl_2]^{\frac{1}{2}}}$$

$$= 1,4 - 0,0592 \log \frac{(3.3 \cdot 10^{-5})}{(3.3 \cdot 10^{-5})^{\frac{1}{2}}}$$

$E = 1,4 - 0,0592 \log (5,75 \cdot 10^{-3}) = 1,53$

$E = 1,53$

Coppia $HClO/ClO^-$

$$HClO \rightleftharpoons H^+ + ClO^- \qquad pK_a = 7.5$$

$$K_a = \frac{[H^+][ClO^-]}{[HClO]} \qquad [H^+] = \frac{K_a \cdot [HClO]}{[ClO^-]}$$

Caso 1 Coppia $[ClO^-] = [HClO]$

$$[H^+] = K_a$$

$$pH = pK_a = 7.5$$

Coppia $HClO/Cl^-$

1

① $HClO + H^+ + e^- \rightleftharpoons \frac{1}{2} Cl_2 + H_2O$

② $\frac{1}{2} Cl_2 + e^- \rightleftharpoons Cl^-$

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③ $HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$

E°_{H} !

$$\Delta G^\circ_{③} = \Delta G^\circ_{①} + \Delta G^\circ_{②}$$

① $HClO + H^+ + e^- \rightleftharpoons \frac{1}{2} Cl_2 + H_2O$.

② $\frac{1}{2} Cl_2 + e^- \rightleftharpoons Cl^-$.

③ $HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$

$E^\circ_{H?} = 1,5V$.

$\Delta G^\circ_{(3)} = \Delta G^\circ_{(1)} + \Delta G^\circ_{(2)}$

$n_3 \cdot E^\circ_{H3} = n_1 E^\circ_{H(1)} + n_2 \cdot E^\circ_{H(2)}$

$E^\circ_{H_3} = \frac{n_1 \cdot E^\circ_{H(1)} + n_2 \cdot E^\circ_{H(2)}}{n_3}$

$E^\circ_{H_3} = \frac{1,59 + 1,40}{2} = 1,5V$

$E_3 = E^\circ_{H_3} - \frac{0,0592}{2} \cdot lg \frac{[Cl^-]}{[H^+][HClO]}$

cond. def $\Rightarrow [Cl^-] = [H^+ Cl O]$

$C_T = 10^{-4} M = [Cl^-] + [HClO] \gg 2[Cl_2] + [ClO^-]$

$2[Cl^-] = 10^{-4} M \quad [Cl^-] = 5 \cdot 10^{-5} M$

$[HClO] = C_T - [Cl^-] = 10^{-4} - 5 \cdot 10^{-5}$

$\simeq 5 \cdot 10^{-5} M$

$E_3 = E^\circ_{H_3} - \frac{0,0592}{2} \cdot \log \frac{[Cl^-]}{[H^+][HClO]}$

$\simeq 1,5 - \frac{0,0592}{2} \cdot \log \frac{5 \cdot 10^{-5}}{[H^+] \cdot 5 \cdot 10^{-5}}$

$E \simeq 1,5 - 0,29\ pH$

Courbe ClO^-/Cl^-

~~$HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$~~

$ClO^- + H^+ \rightleftharpoons$ ~~$HClO$~~

$ClO^- + 2H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$

③ $HClO + H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$.

④ $ClO^- + H^+ \rightleftharpoons HClO$

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⑤ $ClO^- + 2H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$

$$\Delta G^\circ_5 = \Delta G^\circ_3 + \Delta G^\circ_4$$

$$-n_5 \cdot F \cdot E^\circ_{H_5} = -n_3 F \cdot E^\circ_{H_3} + RT \ln K_4$$

$$E^\circ_{H_5} = \frac{n_5 \cdot F E^\circ_{H_3}}{n_5 F} + \frac{RT \ln K_4}{n_5 F}$$

$$= \frac{2 \times 1{,}5}{2} + \frac{0{,}059 \log (10^{-25})}{2}$$

$$E^\circ_{H_5} = 1{,}28\ V$$

$$E_5 = E^\circ_5 - \frac{0{,}059}{2} \log \frac{[Cl^-]}{[H^+]^2 \cdot [ClO^-]}$$

$$[Cl^-] + [ClO^-] \gg 2[Cl_2] + [HClO] = 10^{-4}$$

$$2[Cl^-] = 10^{-4} \qquad [Cl^-] = 5 \cdot 10^{-5}$$

$$[HO^-] = C_T - [H^+] = 10^{-4} - 5\cdot10^{-5} = 5\cdot10^{-5}$$

$$E_S = E^\circ_{H_2S} - \frac{0{,}0592}{2} \lg \frac{5\cdot10^{-5}}{[H^+]^2 \cdot 5\cdot10^{-5}}$$

$$E_S = 1{,}28 - 0{,}592\, pH$$

$$\frac{C_{OH^-}}{C_{HO^-}}$$

C_T $10^{-3}M$ $CH_4 - C - H_2O - CO_2$

H_2CO_3 / HCO_3^- Courbe

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$$K_{a_1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$[H_2CO_3] = [HCO_3^-]$

$$[H^+] = K_{a_1} \frac{[H_2CO_3]}{[HCO_3^-]}$$

$$\boxed{pH = -\log K_{a_1} = 6,4}$$

$HCO_3^- / CO_3^=$ Courbe

$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

$[CO_3^=] = [HCO_3^-]$ $\quad K_{a_2} = \frac{[H^+][CO_3^=]}{[HCO_3^-]}$

$$pH = -\log K = 10,3$$

H_2CO_3 / C

$C + 3H_2O \rightleftharpoons H_2CO_3 + 4H^+ + 4e^-$

$C: 0 \rightarrow +4$

$E^\circ = 0{,}299\ V$

$$E = E^\circ_H + \frac{0{,}0592}{4} \log \frac{[H^+]^4 \cdot [H_2CO_3]}{c^\circ}$$

$c_T = \Sigma c \simeq [H_2CO_3] = 10^{-3}\ M$

$$= 0{,}299 + \frac{0{,}0592}{4} \log (10^{-3}) - 0{,}0592 \cdot pH$$

$$E = 0{,}184 - 0{,}0592\ pH$$

HCO_3^- / C (graphite) Carbone $E_H^\circ = 0{,}324\ V$

$$C + 3H_2O \rightleftharpoons HCO_3^- + 5H^+ + 4e^-$$

$$C_T = \Sigma C \approx [HCO_3^-] = 10^{-3}\ M$$

$$E_H = E_H^\circ + \frac{0{,}059}{4} \log \frac{[HCO_3^-] \cdot [H^+]^5}{C_T}$$

$$\simeq 0{,}324 + \frac{0{,}059}{4} \log(10^{-3}) - \frac{0{,}059}{4} \cdot 5\,pH$$

$$E_H \simeq 0{,}28 - 0{,}074\,pH$$

$CH_4 \longrightarrow C + 4H^+ + 4e^-$

(+4) (0)

$E^\circ = 0{,}0898$ ✓

$[CH_4] = \varepsilon C = C_T = 10^{-3}$

$$E = E^\circ_{H} + \frac{0{,}0592}{4} \log \frac{[H^+]^4 \cdot [C]}{[CH_4]_{eq}}$$

$$= 0{,}0898 + \frac{0{,}0592}{4} \log(10^{-3}) - \frac{0{,}0592}{4} \cdot 4 \cdot pH$$

$$E = 0{,}134 - 0{,}0592\ pH$$

$$CH_4 + 3H_2O \rightleftharpoons CO_3^{=} + 10H^+ + 8e^-$$

$$E^\circ = 0{,}283\ V$$

$$E = E^\circ_H + \frac{0{,}0592}{8} \log \frac{[H^+]^{10}\,[CO_3^{=}]}{[CH_4]\,[H_2O]^3}$$

$$[CH_4] = [CO_3^{=}]$$

$$= 0{,}283 + \frac{0{,}0592}{8} + \frac{0{,}0592}{8} \log [H^+]^{10}$$

$$= 0{,}283 - 0{,}074\ pH$$