

Ex N°6 P92.

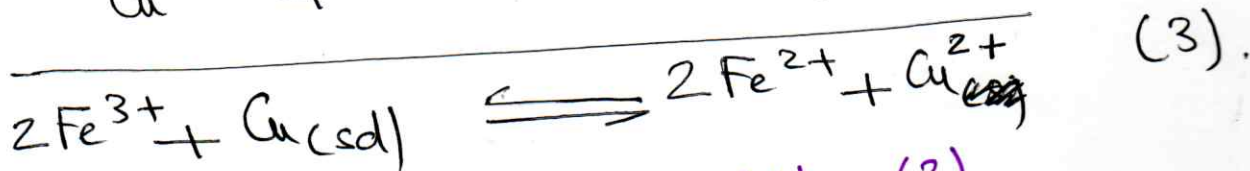
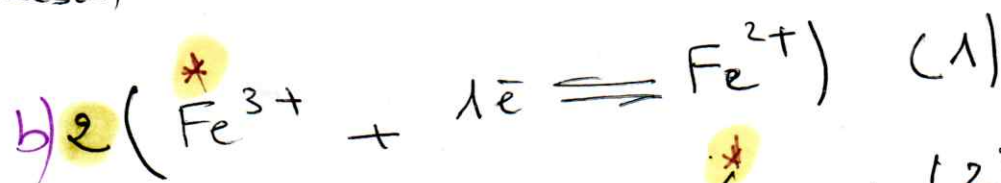
1) a) $E^{\circ}_{\text{Cu}^{2+}/\text{Cu(s)}} = 0,34 \text{ V}$

$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0,77 \text{ V}$

$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} > E^{\circ}_{\text{Cu}^{2+}/\text{Cu(s)}}$ donc

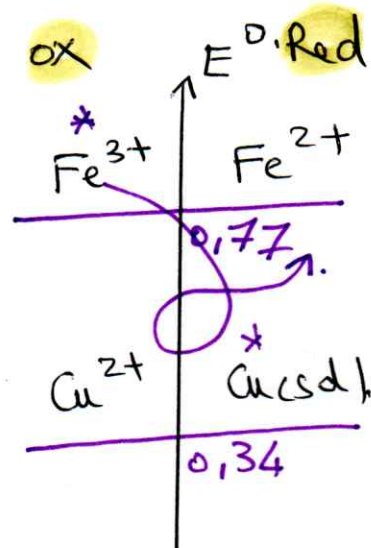
Fe^{3+} est l'oxydant le plus fort.

Cu(s) " le réducteur " " "



$(3) = 2 \times (1) - (2)$.

c) R° limitée $K \ll$.
 R° pratiquement totale K de l'ordre de $10^3, 10^4$.
 R° totale. $K \gg 10^4$



$$\Delta G_3^\circ = 2 \Delta G_1^\circ - \Delta G_2^\circ$$

$$-RT \Delta_m K = 2 (-FE^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}) - (-2FE^\circ_2)$$

$$-RT \ln K = -2F(E_1^{\circ} - E_2^{\circ}).$$

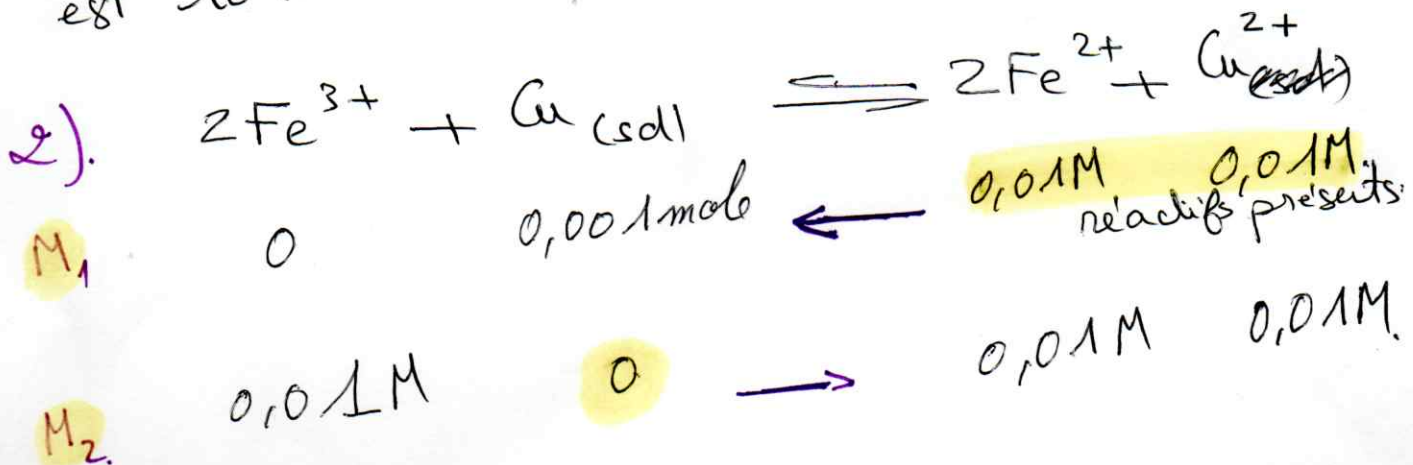
$$\frac{RT}{F} \ln K = 2 (E_1^\circ - E_2^\circ).$$

$$0,06 \log K = 2(E_1^{\circ} - E_2^{\circ})$$

$$K = 10 \frac{2(0,77 - 0,34)}{0,06}$$

$$K = 2,15 \cdot 10^{14} \Rightarrow \Rightarrow \text{La R}^0$$

est totals.



$$a) \quad \pi_{M_1} = \frac{[Fe^{2+}]^2 [Cu^{2+}]}{[Fe^{3+}]^2} \quad a_{Cu(s)} = 1.$$

$$= \frac{0,01^2 \cdot 0,01}{0,02^2} \rightarrow \infty \Rightarrow \pi_{M_1} > K.$$

$\Rightarrow$ La R^0 évolue $\rightarrow$ le sens inverse.
(il faut vérifier que vous avez les réactifs)!!

$$\pi_{M_2} = \frac{0,01^2 \times 0,01}{0,02^2} = 0,01 < K.$$

Pas d'évolution car on a absence de $Cu(s)$!

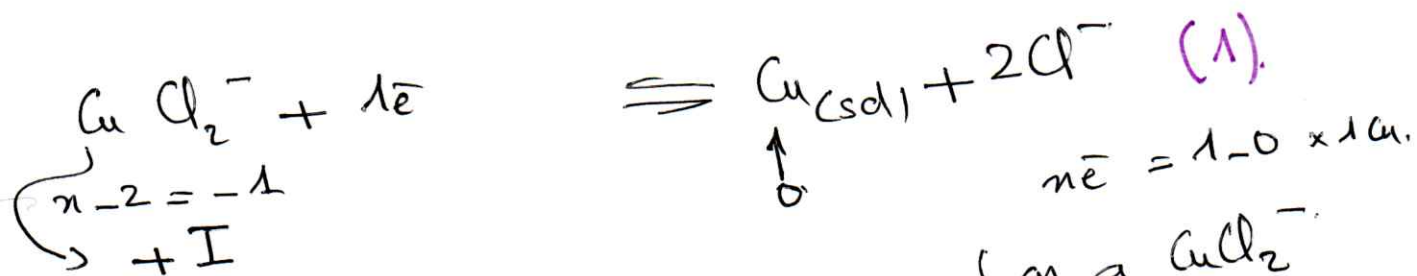
b) M_1 : équilibre dynamique (on a évolution)

M_2 : équilibre statique (pas d'évolution).

3). a) on observe un dépôt de $Cu(s)$,

b) si on ajoute $Cu(s)$, la R^0 se déplace $\rightarrow$ le sens direct.

* $E^\circ_{\text{CuCl}_2^-/\text{Cu(s)}} = \beta$ (données).



$(1) = -(2) + (3)$

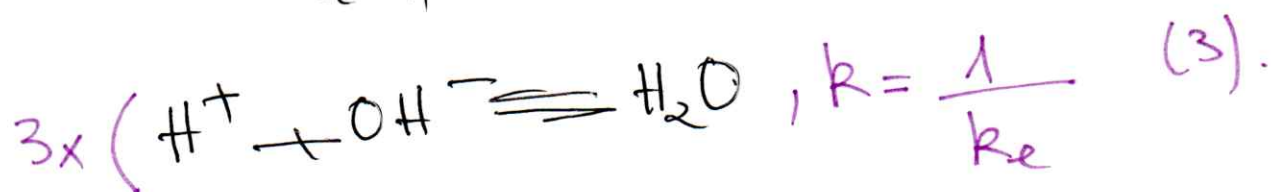
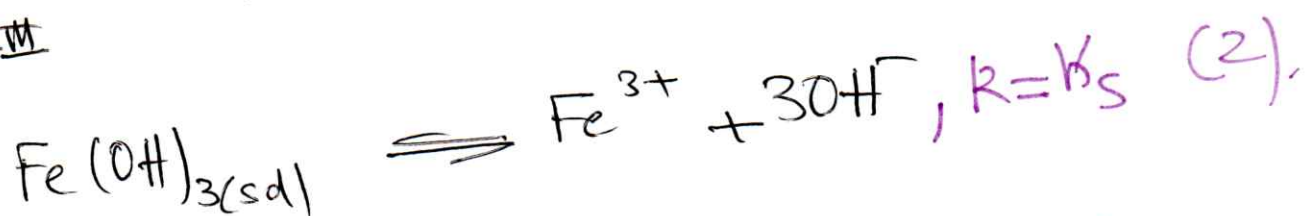
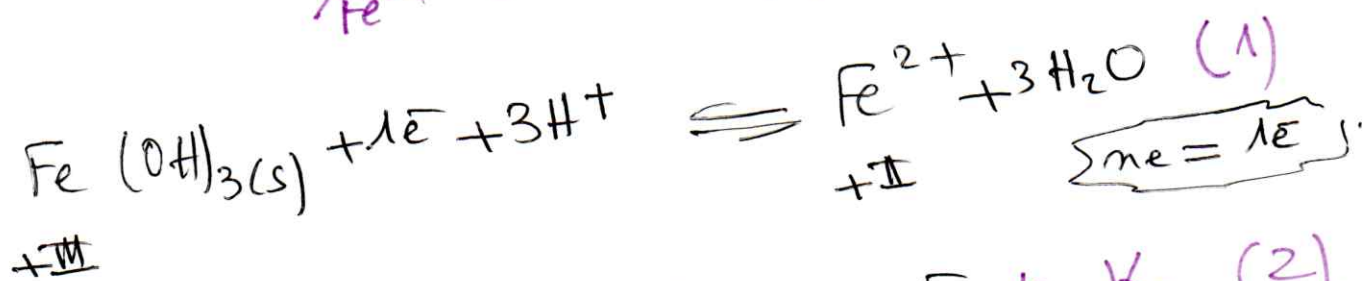
→ $\Delta G^\circ_1 = \Delta G^\circ_3 - \Delta G^\circ_2$

$$-F E^\circ_{\text{CuCl}_2^-/\text{Cu}} = -F E^\circ_{\text{Cu}^+/\text{Cu(s)}} - (-RT \ln K_f)$$

$$E^\circ_{\text{CuCl}_2^-/\text{Cu(s)}} = E^\circ_{\text{Cu}^+/\text{Cu(s)}} - 0,06 \log 10^5$$

$E^\circ_{\text{CuCl}_2^-/\text{Cu(s)}} = 0,22 \text{ V}$

$$* E^{\circ}(\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}) = f(E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}}, K_s \text{ et } K_e).$$



$$(1) = (2) + 3 \times (3) + (4).$$

$$\Delta G^{\circ}_1 = \Delta G^{\circ}_2 + 3\Delta G^{\circ}_3 + \Delta G^{\circ}_4.$$

$$-F E^{\circ}_{\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}} = -RT \ln K_s + 3(-RT \ln \frac{1}{K_e}) - F E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}}.$$

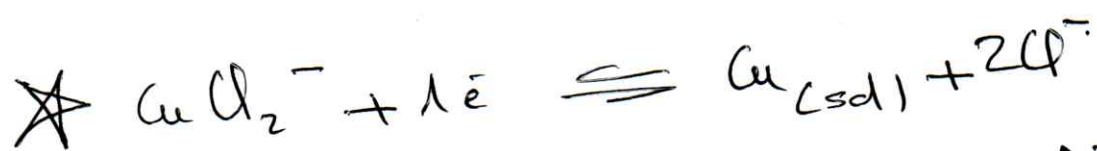
$$E^{\circ}_{\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}} = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + 0,06 \log K_s - 3 \times 0,06 \log K_e.$$

$$E^{\circ}_{\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}} = 0,77 + 0,06 \log 10^{-39} - 0,18 \log 10^{-14}$$

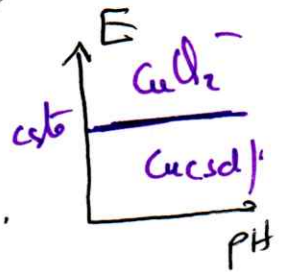
$$E^{\circ}_{\text{Fe}(\text{OH})_3(\text{s})/\text{Fe}^{2+}} = 0,95 \text{ V} !$$

* expression du potentiel d'électrode.

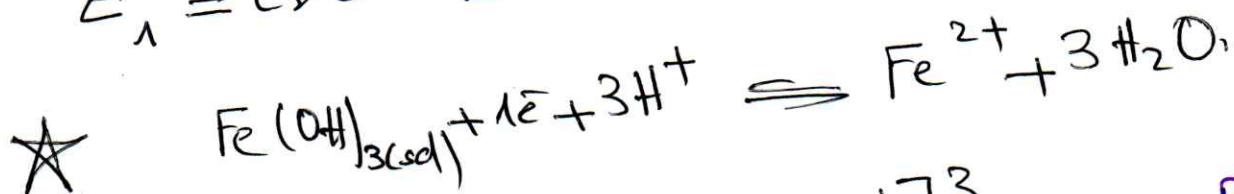
↓ c.i.a.d $\{E_1\}$.



$$E_1 = E_{\text{CuCl}_2^- / \text{Cu}_{(s)}}^0 + 0,06 \log \frac{[\text{CuCl}_2^-]}{[\text{Cl}^-]^2}$$



$E_1 = \text{cste} \Rightarrow$ d'où E_1 ne dépend pas du pH



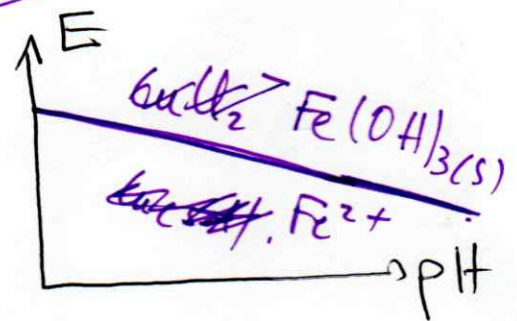
$$E_2 = E_2^0 + 0,06 \log \frac{[\text{H}^+]^3}{[\text{Fe}^{2+}]}$$

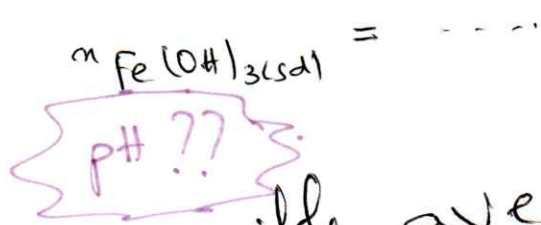
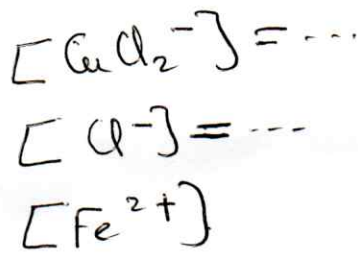
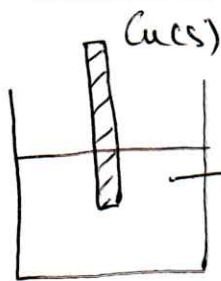
$$\text{pH} = -\log[\text{H}^+]$$

$$= E_2^0 - 0,06 \log[\text{Fe}^{2+}] + 0,18 \log[\text{H}^+]$$

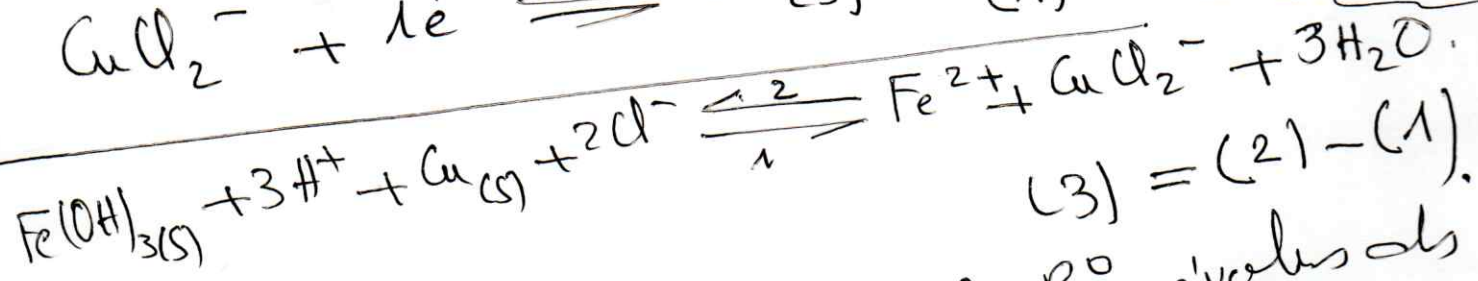
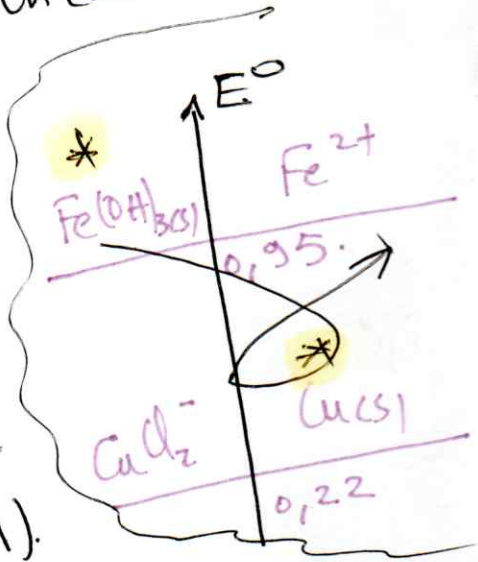
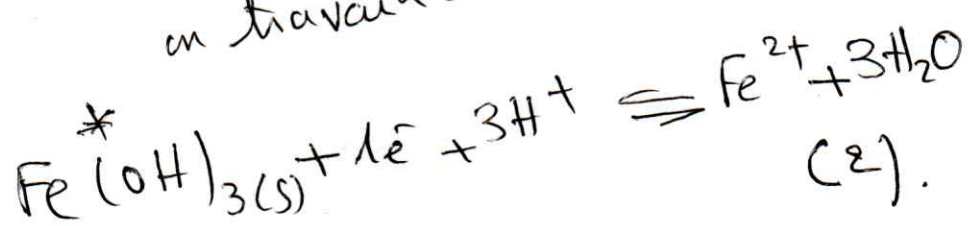
$$E_2 = E_2^0 - 0,06 \log[\text{Fe}^{2+}] - 0,18 \text{pH} !$$

$E_2 \searrow$ lorsque pH $\nearrow$.





a) R^0 (en principe on travaille avec E^0)
 mais la valeur $\rightarrow$ le pH est inconnue $\Rightarrow$ on travaille avec E^0 .



attaque $\rightarrow$ $Cu(s)$ c.a.d la R^0 évolue ds le sens direct: $(\Delta_r G_3 < 0)$. ($Cu(s)$ n'est pas stable!)

$\Delta_r G_3 = \Delta_r G_2 - \Delta_r G_1$
 $= -2F(E_2 - E_1) < 0$
 $\Rightarrow E_2 > E_1$!
 P-7-

$$E_1 = 0,12 \text{ V.}$$

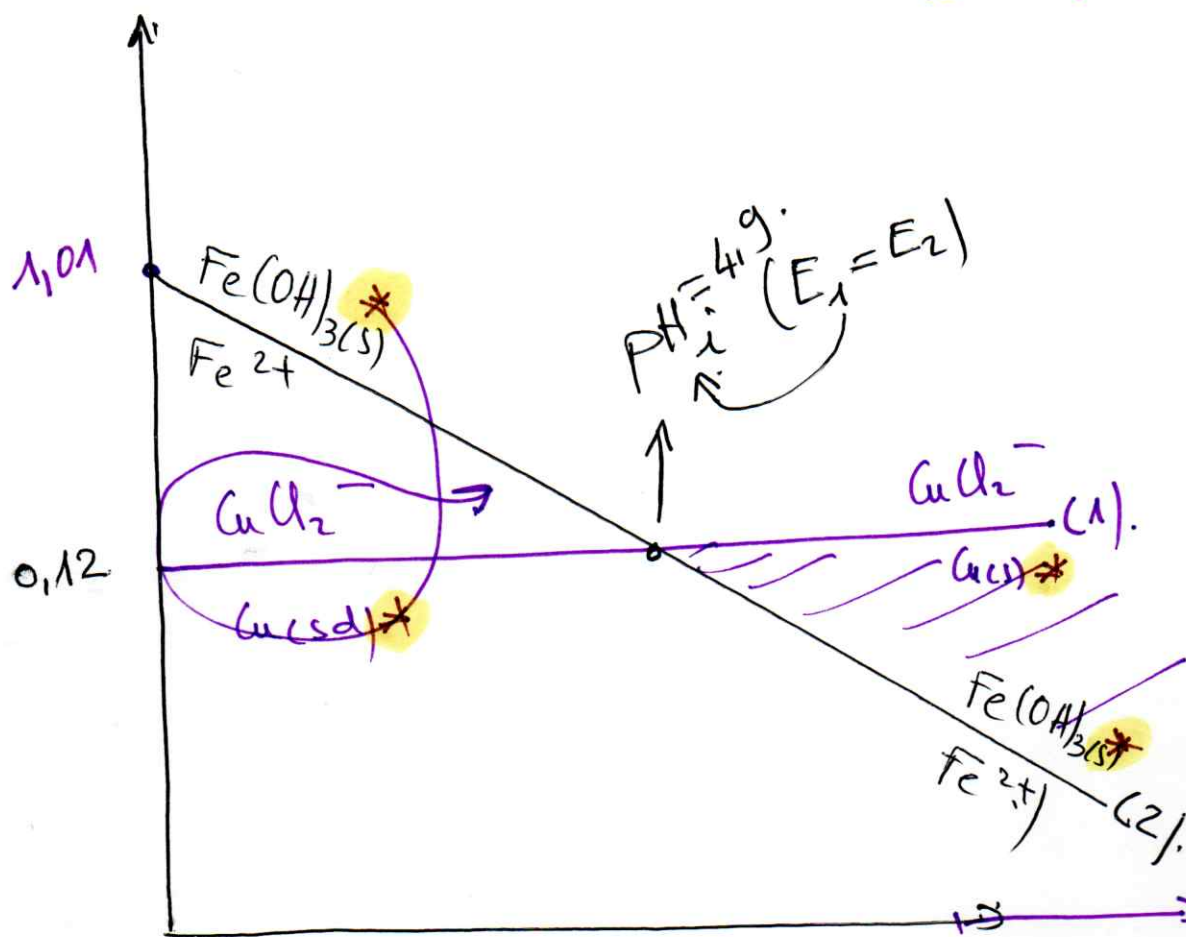
$$E_2 = 1,01 - 0,18 \text{ pH}$$

$$1,01 - 0,18 \text{ pH} > 0,12$$

$$\begin{cases} \text{pH} = 0; E_2 = 1,01 \\ \text{pH} = 10, \\ E_2 = -0,79 \text{ V} \end{cases}$$

$$\Rightarrow \text{pH} < 4,9 !$$

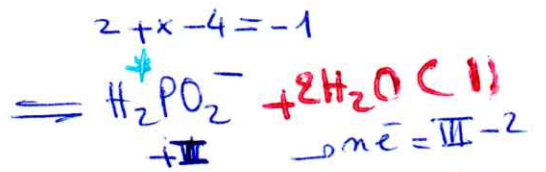
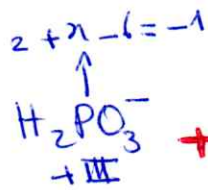
relatif $\text{Cu(s)} \rightarrow (*)$
sur Cu(s)



pour $\text{pH} < 4,9$: on a Cu(s) et $\text{Fe(OH)}_3\text{(s)}$ se trouvent
 ds 2 domaines de stabilité $\neq \Rightarrow$ ils peuvent
 réagir : attaque de $\text{Cu} \Rightarrow \text{Cu n'est pas stable}$
 pour $\text{pH} > 4,9$: Cu(s) et $\text{Fe(OH)}_3\text{(s)}$ se
 trouvent ds le m^{ême} domaine de stabilité
 $\Rightarrow$ pas de R.O.
 $\Rightarrow \text{Cu stable}$

Exercice n° 7 P63

1) couple (1).



$\rightarrow m\bar{e} = \text{III} - 2$

$= 2\bar{e} \rightarrow 1P$

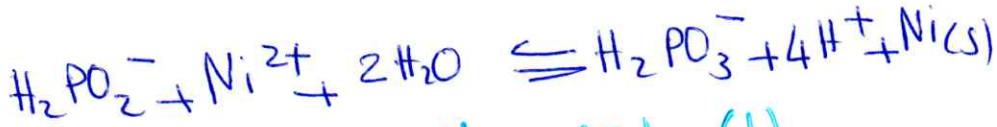
1^{ère} étape.

2^{ème} étape

CH_2O

3^{ème} étape H^+

couple 2



$$(3) = (2) - (1)$$

$$2) \Delta_r G_1 = -2FE_1$$

$$\Delta_r G_2 = -2FE_2.$$

$$3) \Delta_r G_3 = \Delta_r G_2 - \Delta_r G_1$$

$$= -2F(E_2 - E_1)$$

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

$$4) \Delta_r G_3^\circ = -2F(E_2^\circ - E_1^\circ) = -RT \ln K.$$

$$\Rightarrow \frac{RT}{F} \ln K = 2(E_2^\circ - E_1^\circ)$$

$$0,06 \log K = 2(E_2^\circ - E_1^\circ)$$

$$K = 10^{\frac{2(E_2^\circ - E_1^\circ)}{0,06}}$$

La R° est totale.

2^{ème} méthode :

à l'équilibre $\Delta_r G_3 = -2F(E_2 - E_1) = 0$

$$\Rightarrow E_1 = E_2.$$

$$E_1^0 + \frac{0,059}{2} \log \frac{[H_2PO_3^-][H^+]^2}{[H_2PO_2^-]} = E_2^0 + \frac{0,059}{2} \log [Ni^{2+}]$$

$$\text{or } K = \frac{[H_2PO_3^-][H^+]^2}{[H_2PO_2^-][Ni^{2+}]}$$

$$\Rightarrow \frac{0,059}{2} \log K = E_2^0 - E_1^0.$$

$$K = 10^{\frac{0,059}{2} (E_2^0 - E_1^0)}$$

Exercice n° 8

Donnée $\Delta_f G^0 \rightarrow \Delta_r G_{298,15}^0 = \dots$



$$1) F = (C - r - k) + (P - l) \\ = (4 - 0 - 1) + (2 - 2).$$

$$F = 3$$

2) $P_t, y_{O_2}, P_{O_2}??$

Non, car P_t, y_{O_2} et P_{O_2} sont 3 paramètres intensifs
mais $\rightarrow$ dépendants:

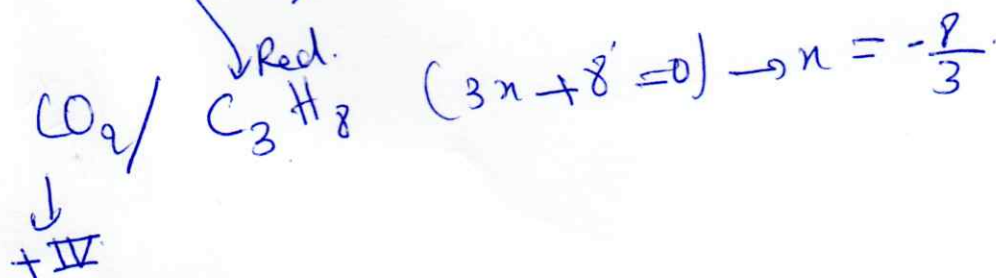
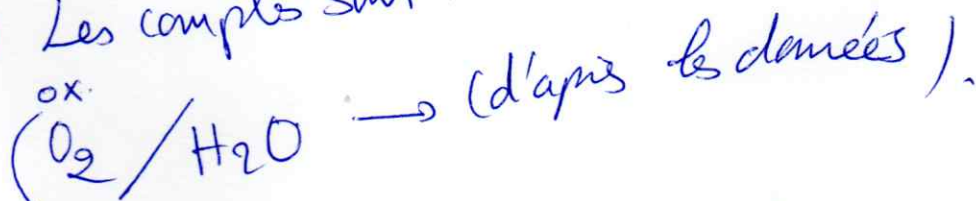
$$P_{O_2} = y_{O_2} \times P_t$$

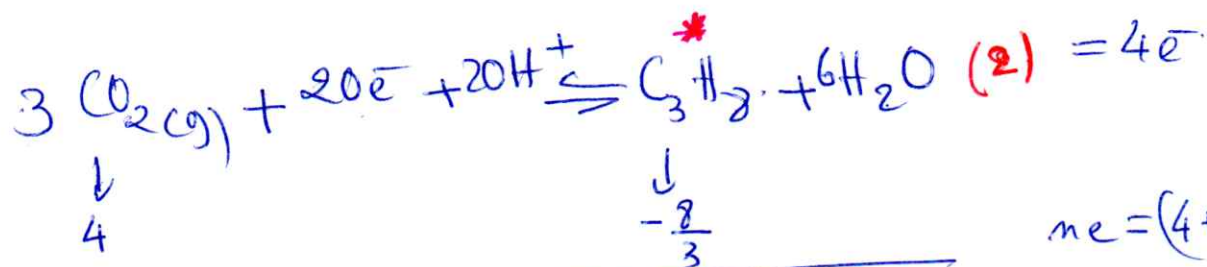
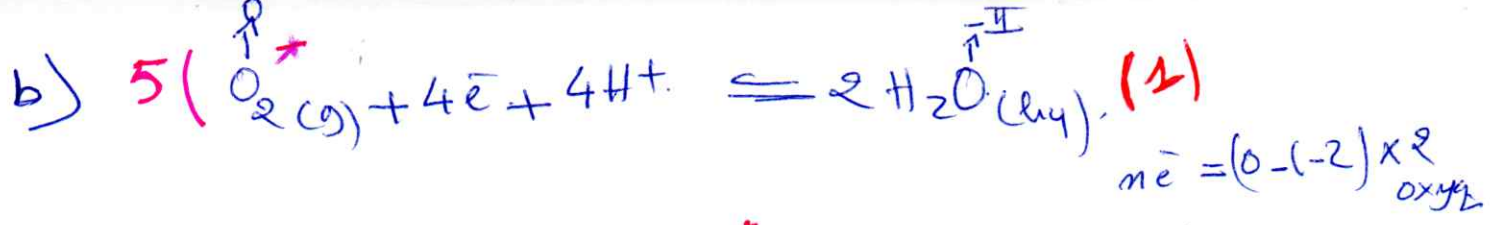
3) $\Delta_r G_{298,1r}^\circ = 3 \Delta_f G^\circ(O_2) + 4 \Delta_f G^\circ(H_2O) - \Delta_f G^\circ(C_3H_8) - 5 \Delta_f G^\circ(O_2)$

$$\Delta_r G_{298}^\circ = 3 \times (-394,4) + 4 \times (-237,1) + 23,14$$

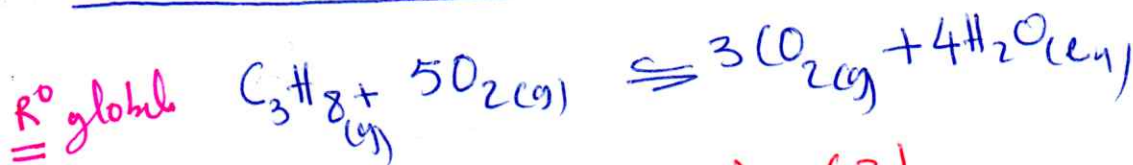
$$\Delta_r G_{298}^\circ = -2108,2 \text{ kJ mol}^{-1}$$

4) a) Les couples sont:





$n\text{e}^- = (4 + \frac{8}{3}) \times 3\text{C}$
 $= \underline{\underline{20\text{e}^-}}$



$(3) = 5 \times (1) - (2)$

5) $\Delta G^\circ_3 = -20\text{F} \Delta E^\circ$

$\Rightarrow \Delta E^\circ = \frac{\Delta G^\circ_3}{-20\text{F}} = \frac{-210812 \times 10^3}{-20 \times 96500}$

$\Delta E^\circ = 1,09 \text{ V}$

$\Delta E^\circ = E^\circ_1 - E^\circ_2 = 1,09$

$\Rightarrow E^\circ_2 = E^\circ_1 - 1,09$

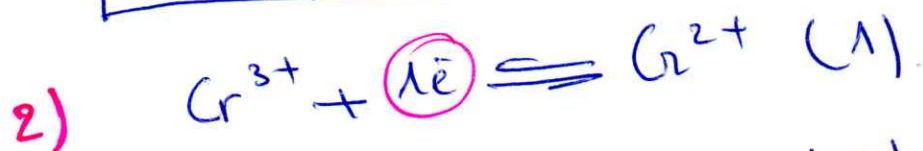
$E^\circ_2 = 1,23 - 1,09$

$E^\circ_2 = 0,14 \text{ V}$

Examination. BG2010

1)

Cr(s)	Cr ²⁺	Cr ³⁺	Cr(OH) ₃ (s)	CrO ₄ ²⁻
0	+II	+III	+III	+VI



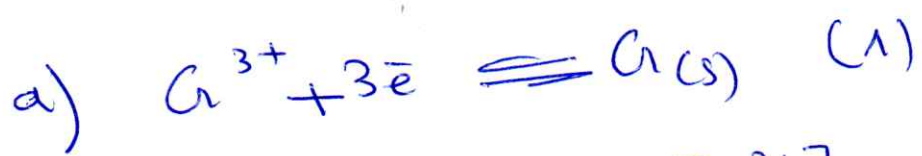
$(1) = (2) - (3) \Rightarrow \Delta G_1^\circ = \Delta G_2^\circ - \Delta G_3^\circ$

$-FE^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -3FE^\circ_{\text{Cr}^{3+}/\text{Cr}} + 2FE^\circ_{\text{Cr}^{2+}/\text{Cr}}$

$E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = 3E^\circ_{\text{Cr}^{3+}/\text{Cr}} - 2E^\circ_{\text{Cr}^{2+}/\text{Cr}}$

A.N: $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = 3 \times (-0,74) - 2(-0,9)$

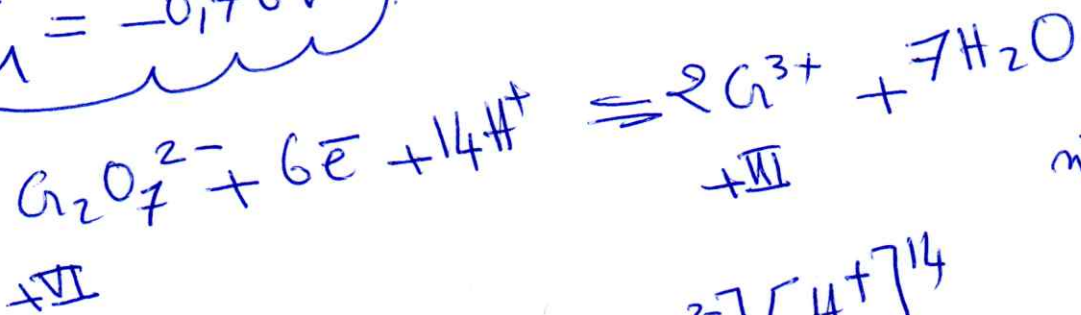
$E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0,42\text{V}$



$$E_{\lambda} = E_{\lambda}^{\circ} + \frac{0,06}{3} \log [Cr^{3+}]$$

$$= -0.74 + 0.02 \log 10^{-1}$$

$$E_1 = -0,76V$$



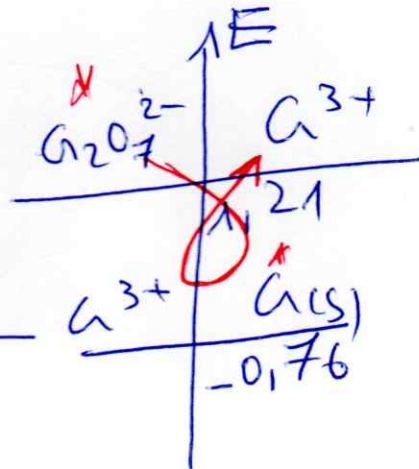
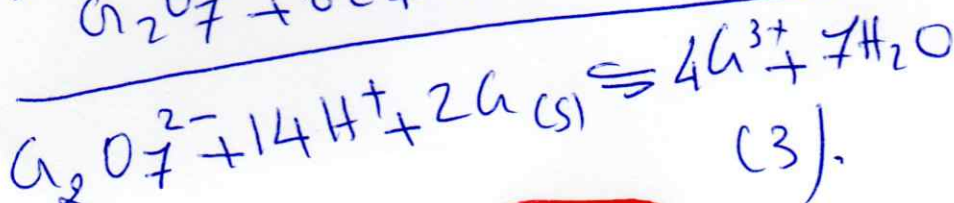
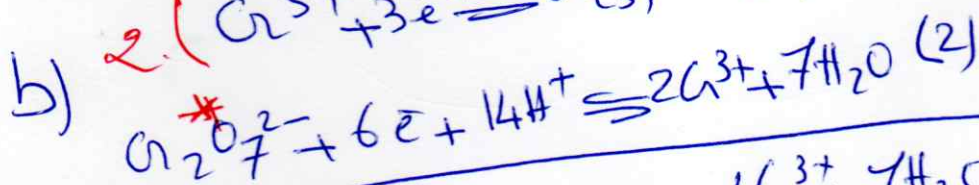
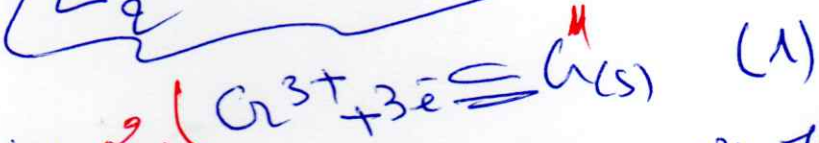
$$n_e = (6-3) \times 2 \downarrow a.$$

$$E_2 = E_2^\circ + \frac{0,06}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

$$= 1.36 + 0.01 \log \frac{10^{-3} (10^{-1})^{14}}{10^{-2}}$$

$$= 1,36 + 0,01 \log^{-1} r.$$

$$E_g = 1.21 \text{ V}$$



P14

$$c) (3) = (2) - 2 \times (1)$$

$$\Delta G_{r3}^{\circ} = -6F(E_2^{\circ} - E_1^{\circ})$$

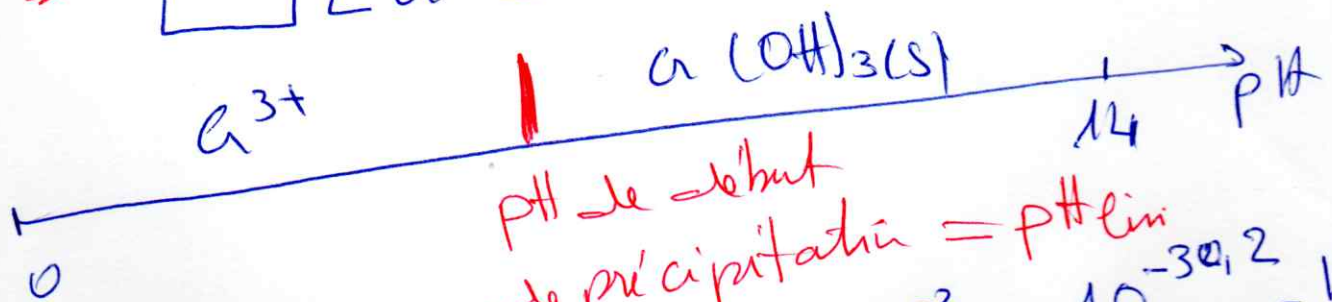
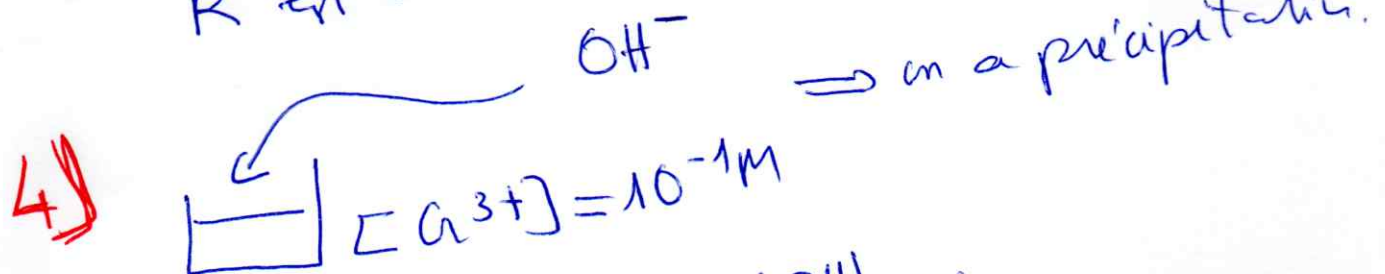
$$= -6 \times 96500 (1,36 + 0,74)$$

$$\Delta G_{r3}^{\circ} = -1215900 \text{ J mol}^{-1}$$

$$d) \Delta G_{r3}^{\circ} = -RT \ln K = -1215900$$

$$\Rightarrow K = \exp \frac{1215900}{8,314 \times 298} \Rightarrow$$

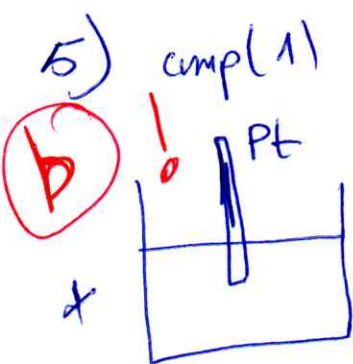
R° et total



$$K_s = [\text{Al}^{3+}][\text{OH}^-]^3 \Rightarrow [\text{OH}^-]^3 = \frac{10^{-30,2}}{10^{-1}} = 10^{-29,2}$$

$$\Rightarrow [\text{OH}^-] = 10^{-9,73} \text{ M} \Rightarrow [\text{H}^+] = 10^{-4,27} \text{ M}$$

$$\text{pH} = 4,27$$



$pH = 1 \rightarrow [H^+] = 10^{-1} M.$

bichromate $[Cr_2O_7^{2-}] = 10^{-2} M.$

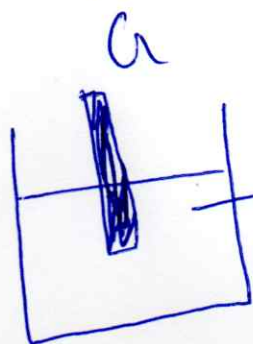
$[Cr^{3+}] = 10^{-1} M.$

$$E_{Cr_2O_7^{2-}/Cr^{3+}} = E^0 + \frac{0,06}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^4}{[Cr^{3+}]^2}$$

$$= 1,36 + 0,01 \log \frac{10^{-2} \cdot 10^{-4}}{(10^{-1})^2}$$

$E_{Cr_2O_7^{2-}/Cr^{3+}} = 1,22 V$

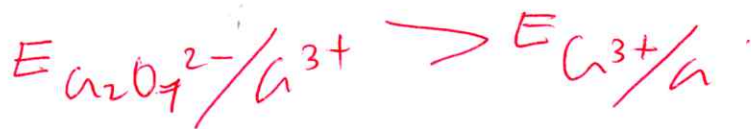
* compa (2).



$[Cr^{3+}] = 10^{-1} M.$

$$E_{Cr^{3+}/Cr} = E^0_{Cr^{3+}/Cr} + \frac{0,06}{3} \log [Cr^{3+}]$$

$E_{Cr^{3+}/Cr} = -0,76 V$

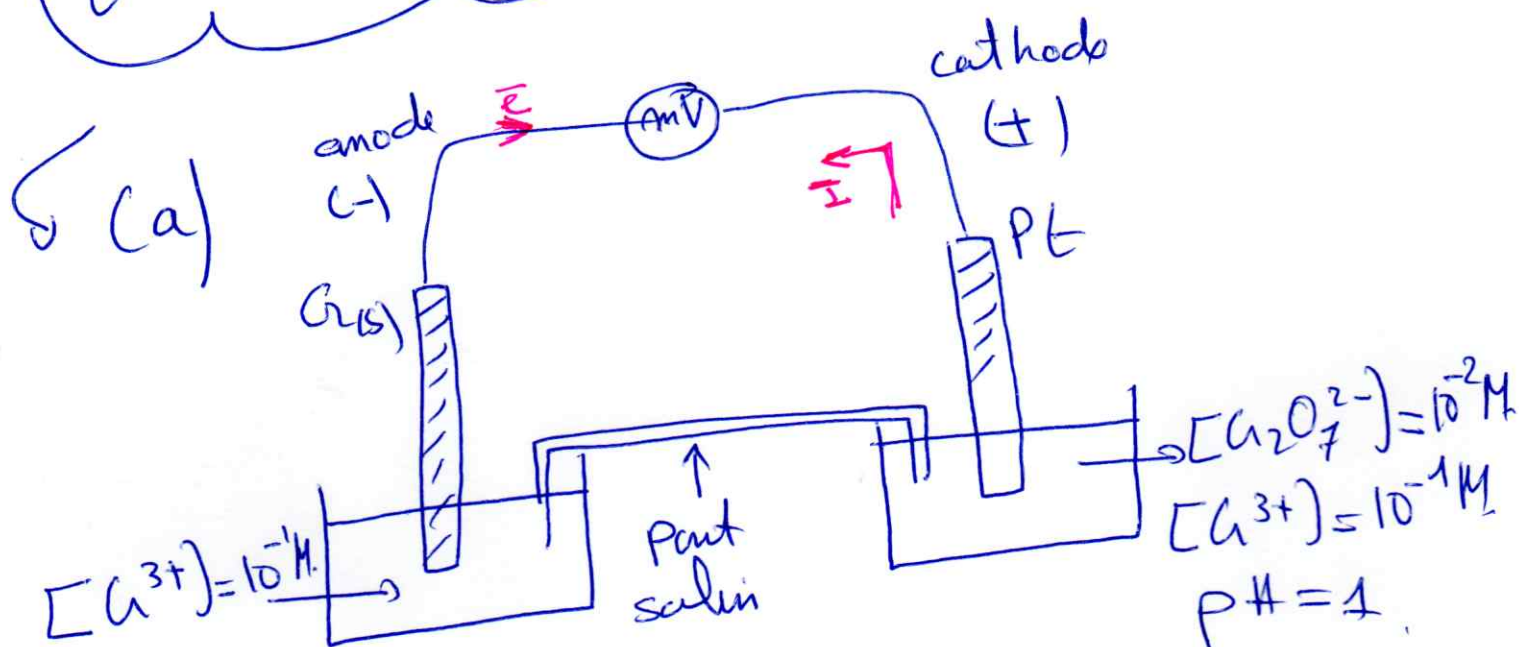


$\downarrow$
Pt, Pol (+)

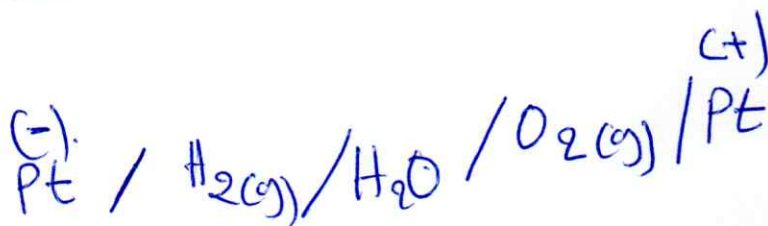
$\downarrow$
 $Cr(s): pol(-)$

$$f.e.m = 1,22 - (-0,76)$$

$$f.e.m = 1,98V$$



E_{xNO}



$$P_{H_2} = 1 atm = P_{O_2}$$

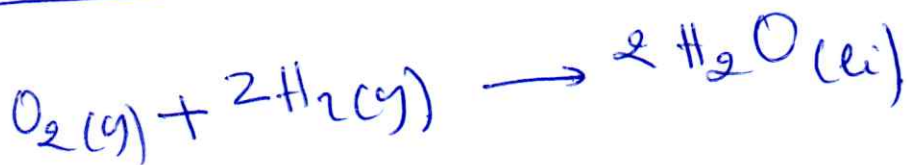
$$f.e.m^{\circ} = E^{\circ} = 1,23V \quad \text{à } T = 25^{\circ}C$$

$$\frac{\partial E^{\circ}}{\partial T} = -840 \mu V \cdot K^{-1}$$

anode (-): oxydation: couple $H^+ / H_2(g)$
 $\xrightarrow{\text{Reduction}}$ oxydation



cathode (+) Reduction: couple $O_2(g) / H_2O$
 $\xrightarrow{\text{Reduction}}$



$$2) \Delta_r G^\circ = -4FE^\circ$$

$$= -4 \times 96500 \times 1,23$$

$$\Delta_r G^\circ = -474780 \text{ J mol}^{-1}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ$$

$$3) \Delta_r S^\circ = -\frac{\partial \Delta_r G^\circ}{\partial T}$$

$$= -\frac{\partial (-4FE^\circ)}{\partial T}$$

$$-840 \times 10^{-6} \text{ V K}^{-1}$$

$$= 4F \left(\frac{\partial E^\circ}{\partial T} \right)$$

$$= 4 \times 96500 \times (-840 \times 10^{-6})$$

$$\Delta_r S^\circ = -324,24 \text{ J K}^{-1}$$

$$\Delta_r H^\circ = -474780 + 289 \times (-324)$$