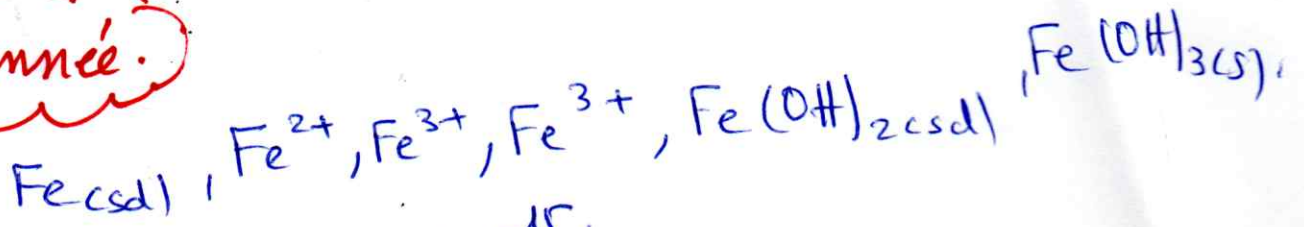


Diagramme de pourbaix E - pH du Fer.

Donnée:



$$K_{s1}(\text{Fe}(\text{OH})_2(\text{s})) = 10^{-15}$$

$$K_{s2}(\text{Fe}(\text{OH})_3(\text{s})) = 10^{-38}$$

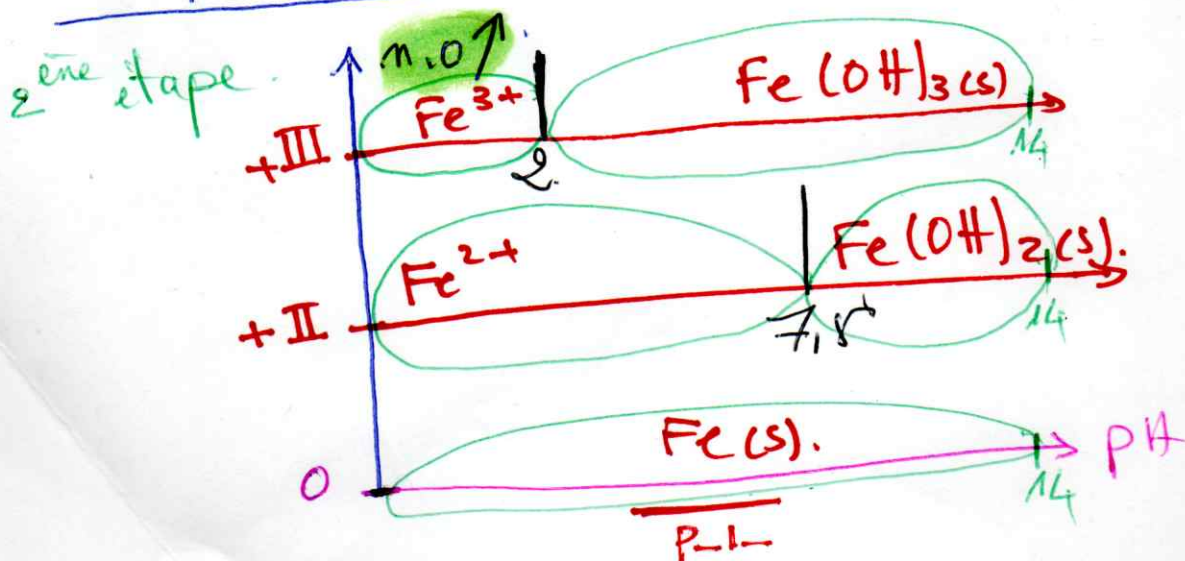
Concentration du trace $C_{\text{tra}} = 10^{-2} \text{ M}$.

$$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0,77 \text{ V} \quad E^{\circ}_{\text{Fe}^{2+}/\text{Fe(s)}} = -0,44 \text{ V}$$

Tracer le diagramme E - pH du Fer:

1^{ère} étape:

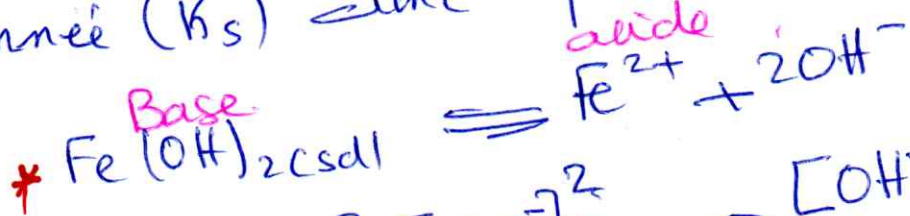
entités	Fe(s)	Fe^{2+}	Fe^{3+}	$\text{Fe}(\text{OH})_2(\text{s})$	$\text{Fe}(\text{OH})_3(\text{s})$
n.o	0	+II	+III	+II	+III



3^{ème} étape

Détermination du pH de début de précipitation
de $\text{Fe}(\text{OH})_2(\text{s})$ et $\text{Fe}(\text{OH})_3(\text{s})$

Donnée (K_s) $\rightarrow$ donc équilibre avec OH^-



$K_{s1} = [\text{Fe}^{2+}][\text{OH}^-]^2 \Rightarrow [\text{OH}^-]_{\text{lim}}^2 = \frac{K_s}{[\text{Fe}^{2+}]}$

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

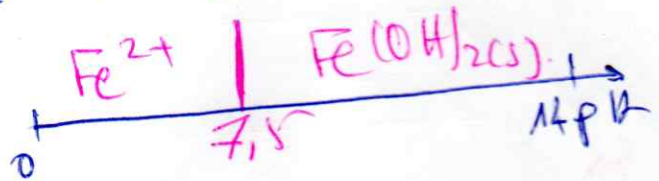
$\Rightarrow 2 \log[\text{OH}^-] = \log K_{s1} - \log C_{\text{tra}}$

$\text{pOH}_{\text{lim}} = \frac{1}{2} (\text{p}K_{s1} + \log C_{\text{tra}})$

$\text{pH}_{\text{lim}1} = \text{p}K_e - \frac{1}{2} (\text{p}K_{s1} + \log C_{\text{tra}})$

A.N $\text{pH}_{\text{lim}1} = 14 - \frac{1}{2} (15 + \log 10^{-2})$

$\text{pH}_{\text{lim}1} = 7,5$



$K_{s2} = [\text{Fe}^{3+}][\text{OH}^-]^3$ / $C_{\text{tra}} = [\text{Fe}^{3+}]$

$\Rightarrow [\text{OH}^-]^3 = \frac{K_{s2}}{C_{\text{tra}}}$

P-2

$$3 \log[\text{OH}^-] = \log K_{s2} - \log C_{\text{tra}}$$

$$\text{pOH} = \frac{1}{3} (\text{p}K_{s2} + \log C_{\text{tra}})$$

$$\text{pH}_{\text{li}} = \text{p}K_e - \frac{1}{3} (\text{p}K_{s2} + \log C_{\text{tra}})$$

A.N. $\text{pH}_{\text{li2}} = 14 - \frac{1}{3} (38 + \log 10^{-2})$

$$\underline{\underline{\text{pH}_{\text{li2}} = 2}}$$

3ème étape: détermination des couples ox/red.

$+III/+II$ (on a 3 couples).

$$0 \leq \text{pH} \leq 2$$

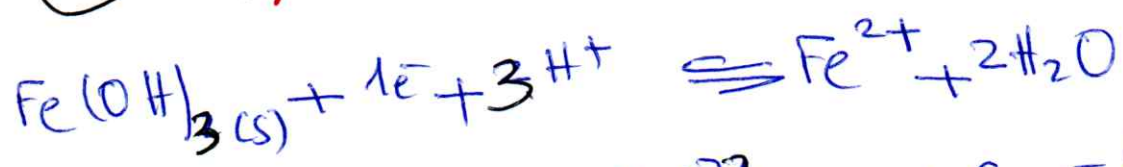


$$E_1 = E_1^0 + 0,06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\left\{ \begin{array}{l} C_{\text{tra}} = [\text{Fe}^{3+}] + [\text{Fe}^{2+}] \\ \text{à la braker} \\ [\text{Fe}^{3+}] = [\text{Fe}^{2+}] = \frac{C_{\text{tra}}}{2} \end{array} \right.$$

$$\Rightarrow \text{pH}_{\text{li2}} = 0,77 \text{V}$$

$$(2) \leq pH \leq 7,5.$$



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

$$= E_2^0 - 0,06 \log 10^{-2} + 0,18 \log [H^+]$$

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

$$E_2 = E_2^0 + 0,12 - 0,18 pH$$

$E_2^0 ??$
par continuité.

pour $pH = 2$ on a $E_1 = E_2$

$$\Rightarrow E_2^0 + 0,12 - 0,12 pH = 0,77.$$

$$\Rightarrow E_2^0 = 0,77 - 0,12 + 0,18 \times 2.$$

$$E_2^0 = 0,29 \quad 1,01$$

$$\Rightarrow E_2 = 1,43 - 0,18 pH \text{ (V)}$$

$$\left. \begin{array}{l} pH = 7,5 \\ E_2 = 0,29 \text{ V} \end{array} \right\}$$

$$2 \leq pH \leq 14$$



$$E_3 = E_3^0 + 0,06 \cdot \log[H^+] = E_3^0 - 0,06 \text{ pH}$$

Détermination de E_3^0 ??

$$\text{pH} = 4,5 \text{ m } E_2 = E_3.$$

$$\Rightarrow -0,22 = E_3^0 - 0,06 \times 4,5 \Rightarrow E_3^0 = 0,56.$$

$$\Rightarrow E_3 = 0,56 - 0 \quad \left(E_3 = 0,23 - \underbrace{0,06 \text{ pH (V)}}_{\text{petite}} \right)$$

$$+II/0 \quad 0 \leq \text{pH} \leq 7,5.$$

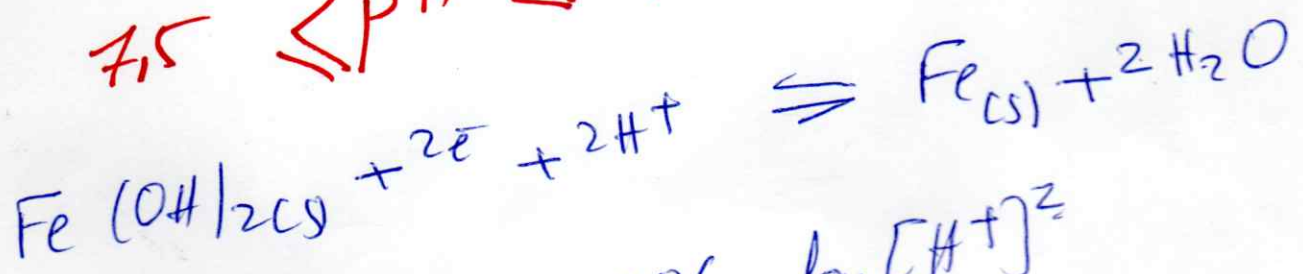


$$E_4 = E_4^0 + \frac{0,06}{2} \log[\text{Fe}^{2+}] \quad / \quad C_{\text{Fe}} = [\text{Fe}^{2+}]$$

$$= -0,44 + 0,03 \log 10^{-2}$$

$$E_4 = -0,5 \text{ V}$$

$$7,5 \leq \text{pH} \leq 14$$



$$E_5 = E_5^0 + \frac{0,06}{2} \log [H^+]^2$$

$$E_s = E_s^0 + 0,06 \log [H^+]$$

$$E_s = E_s^0 - 0,06 \text{ pH}$$

$$\text{pH} = 7,1 \Rightarrow E_s = E_4$$

$$\Rightarrow E_s - 0,06 \text{ pH} = -0,15$$

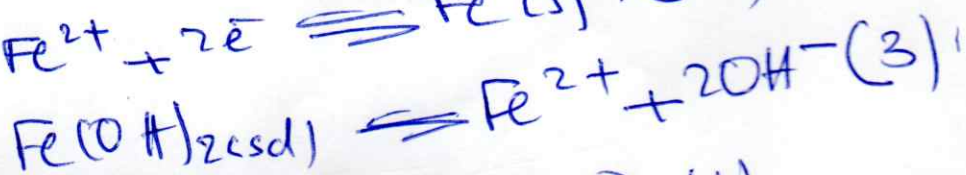
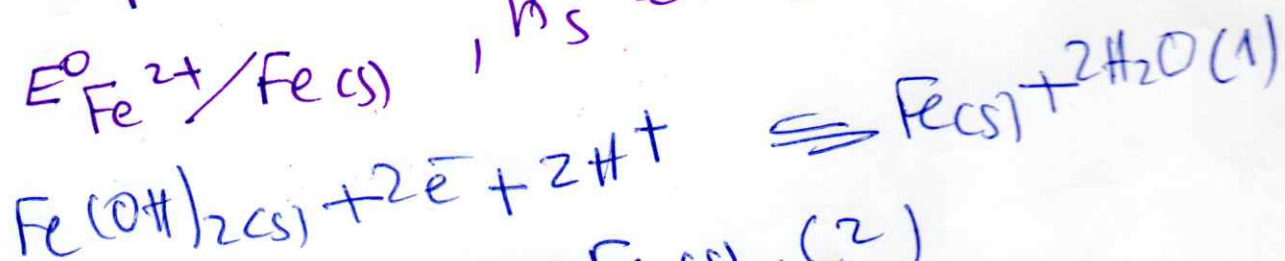
$$\Rightarrow E_s^0 = -0,15 + 0,06 \times 7,1$$

$$= -0,05$$

$$\Rightarrow E_s = -0,05 - \frac{0,06 \text{ pH}}{\text{pente}}$$

Rq les 2 frontières (3) et (5) sont // car elles possèdent la même pente (-0,06)

Rq Exprimer $E^0(\text{Fe}(\text{OH})_2\text{cs})/\text{Fe}(\text{cs})$ en fonction de $E^0_{\text{Fe}^{2+}/\text{Fe}(\text{cs})}$, K_s et K_e .



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

$$\Delta G_1^0 = \Delta G_3^0 + 2\Delta G_4^0 + \Delta G_2^0$$

$$\downarrow$$

$$-2FE_s^0 = -RT \ln K_s + 2 \left(-RT \ln \frac{1}{K_e} \right) - 2FE_{Fe^{2+}/Fe}^0$$

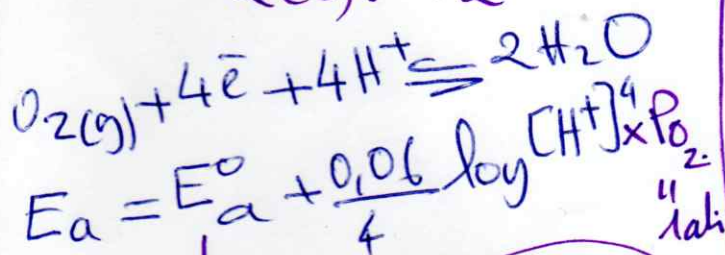
$$E_s^0 = E_{Fe^{2+}/Fe}^0 + 0,03 \log K_s - 0,06 \log K_e$$

A.N $E_s^0 = -0,4 + 0,03 \log 10^{-11} - 0,06 \log 10^{-14}$

$$E_s^0 = -0,05 V$$

Diagramme de l'eau.

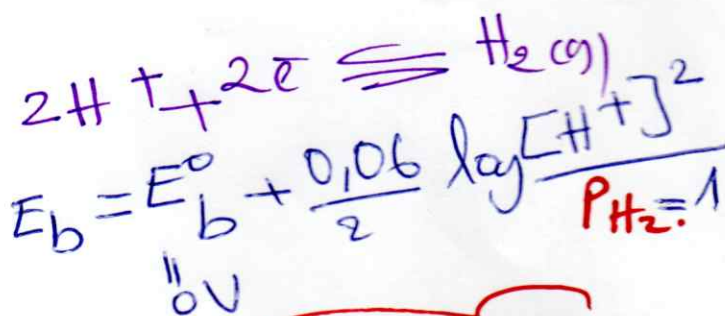
$O_2(g)/H_2O$



$$E_a = E_a^0 + \frac{0,06}{4} \log [H^+]^4 \times P_{O_2}$$

$$E_a = 1,23 - 0,06 pH(V)$$

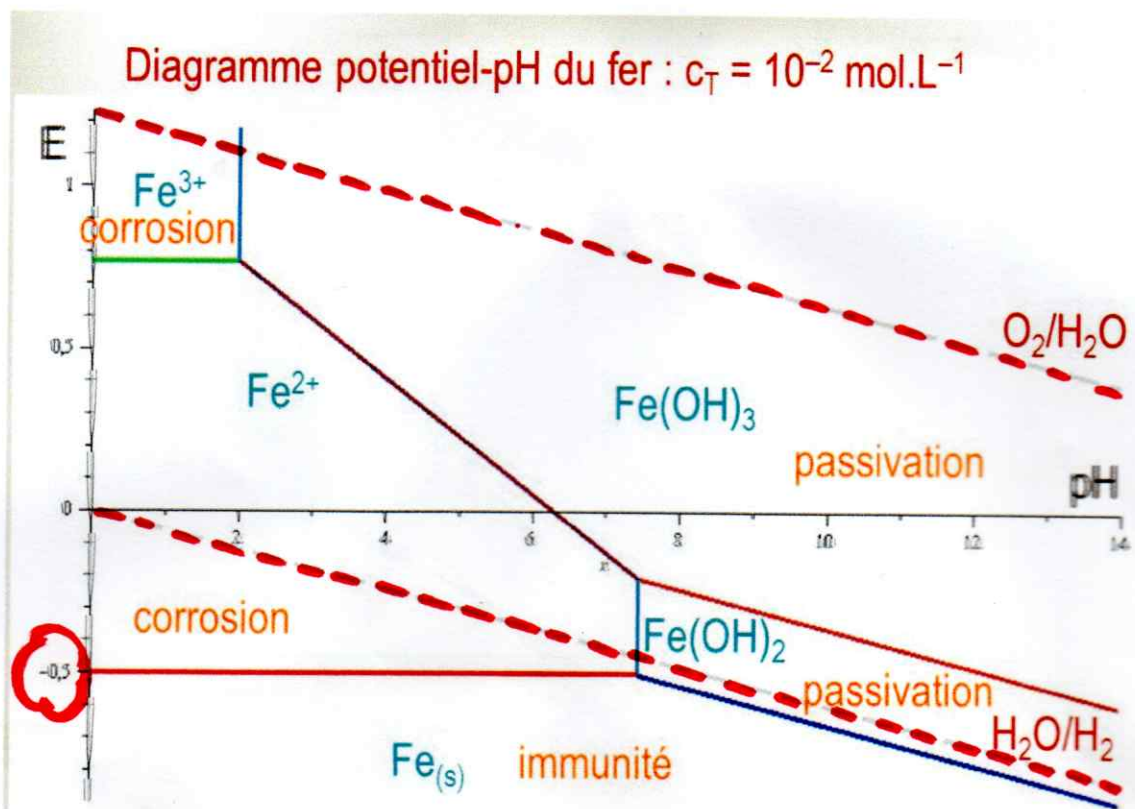
$H_2O/H_2(g) = H^+/H_2$



$$E_b = E_b^0 + \frac{0,06}{2} \log [H^+]^2$$

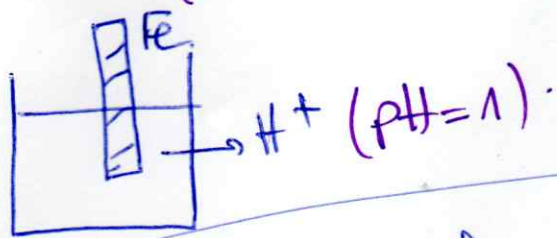
$P_{H_2} = 1$

$$E_b = -0,06 pH$$

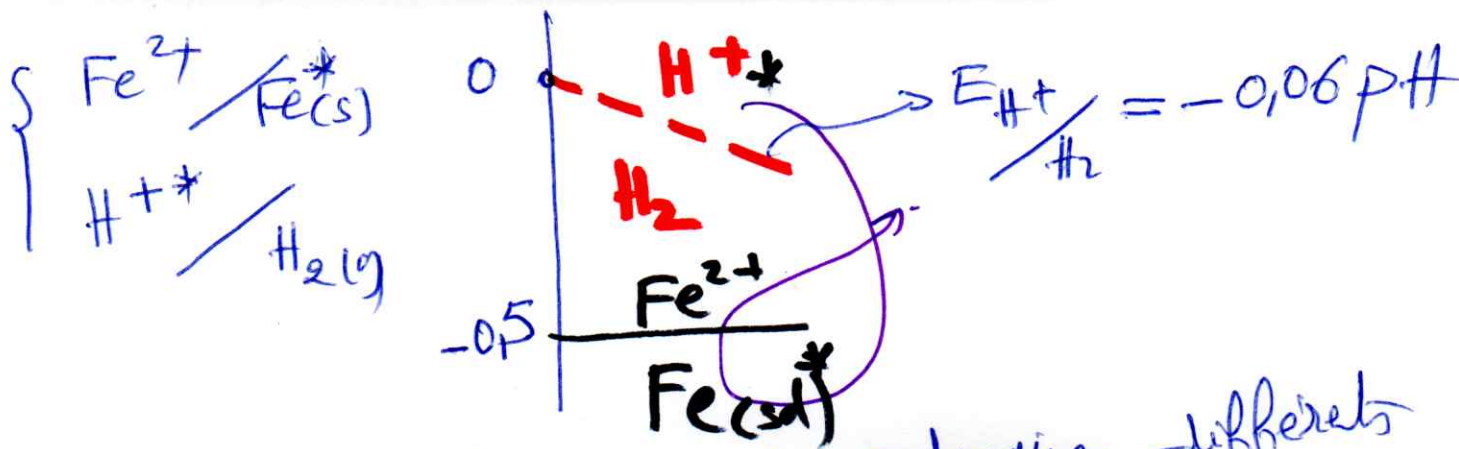


Questions.

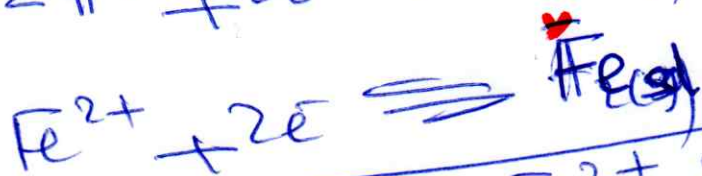
1) une plaque de Fer est-elle stable dans un milieu acide ($\text{pH} = 1$). on a 2 couple. } couple du Fer.
couple de H_2O



Rq Fe joue le rôle que un réducteur.
 $\Rightarrow \text{H}^+$ doit être un oxydant.
 d'après le diagramme on a 2 couples pour Fe(s)
 ou $\text{Fe(OH)}_2/\text{Fe(s)}$ ou $\text{Fe(OH)}_3/\text{Fe(s)}$
 $\text{Fe}^{2+}/\text{Fe(s)}$
 $\text{pH} = 1 \rightsquigarrow$
 $\text{pH} > 7, \text{pH} > 11$
 P-8-



H^+ et $Fe(s)$ se trouvent dans 2 domaines différents
donc ils peuvent réagir ($\Delta_r G < 0$).



justification. $\Delta_r G_3 = -2F \Delta E$

$$\Delta_r G_3 = -2 \times 96500 (E_{H^+/H_2} - E_{Fe^{2+}/Fe})$$

$$E_b = -0.06 \text{ pH} = -0.06$$

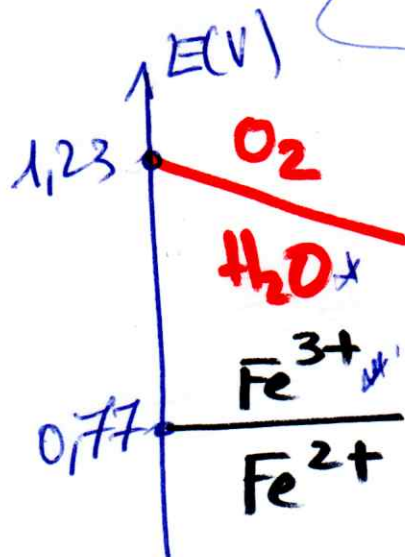
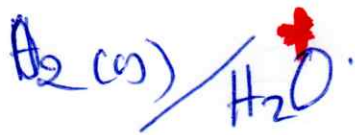
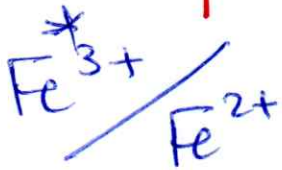
$$= -2 \times 96500 (-0.06 + 0.5)$$

$< 0 \Rightarrow$ la R° évolue dans
sens direct

Les ions Fe^{3+} sont ils stables dans un milieu aqueux (H_2O).

Fe^{3+} est très ox.
donc H_2O doit être Red

⇒ Les couples.



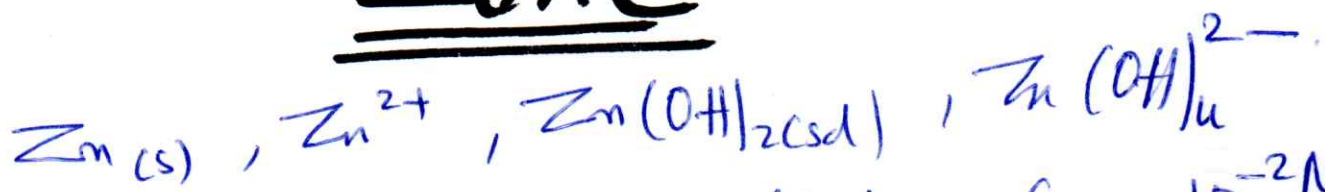
Fe^{3+} et H_2O se trouvent dans le même domaine de stabilité ⇒ donc ils ne peuvent pas réagir ($\Delta_r G > 0$) ⇒ Les ions Fe^{3+} sont stables.

$$\Delta_r G = -nF(\Delta E) < 0$$

$$= -nF \left(E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\text{ox}} - E_{\text{O}_2/\text{H}_2\text{O}} \right)$$

$$\Delta_r G > 0.$$

Zinc



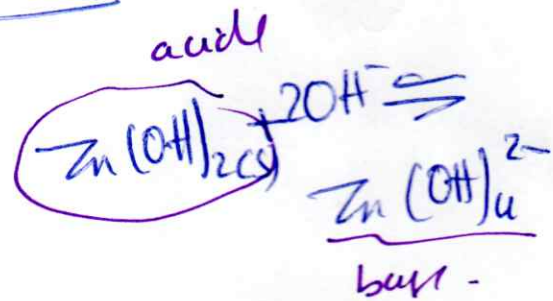
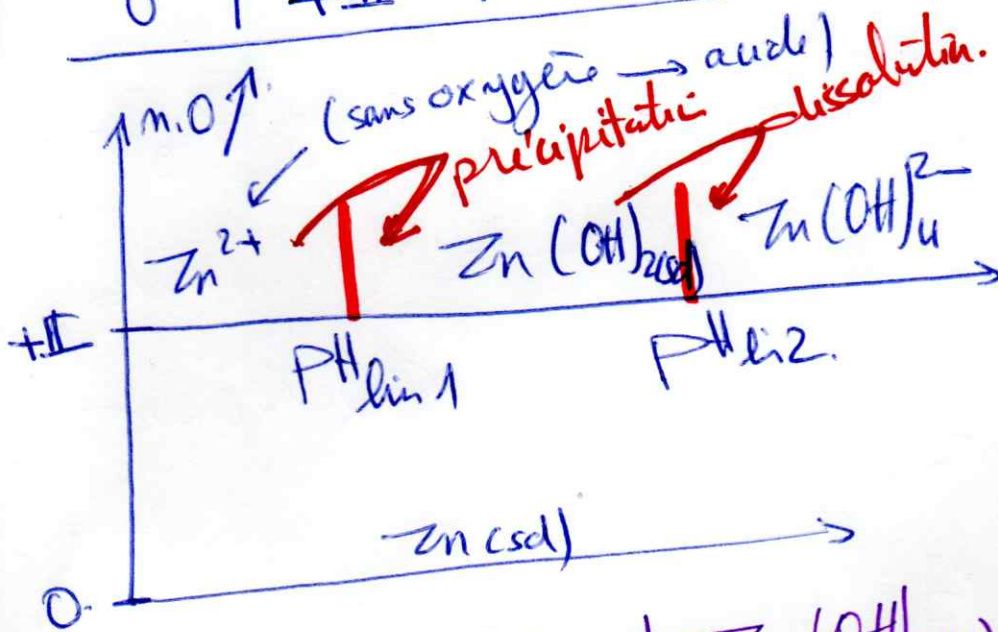
$E_{Zn^{2+}/Zn(s)}^\circ = -0,76 V$ $C_{Zn} = 10^{-2} M$ réactif.

$pK_s(Zn(OH)_2(csd)) = 16,35$

β : cste $\rightarrow$ dissolution $\rightarrow Zn(OH)_2(csd)$

$\rightarrow$ un milieu Basique

$Zn(s)$	Zn^{2+}	$Zn(OH)_2(csd)$	$Zn(OH)_4^{2-}$
0	+II	+II	+II



* entre Zn^{2+} et $Zn(OH)_2(csd)$: on a précipitation

$$Zn(OH)_2(csd) \rightleftharpoons Zn^{2+} + 2OH^-$$

$$K_s = \frac{[Zn^{2+}][OH^-]^2}{C_{Zn}} \Rightarrow [OH^-]_{lin}^2 = \frac{K_s}{C_{Zn}}$$

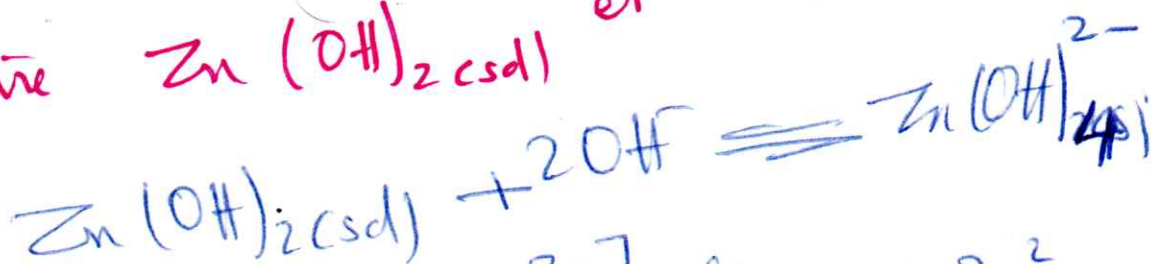
$$\log[\text{OH}^-] = \log K_s - \log C_{\text{tr}}$$

$$\text{pOH} = \frac{1}{2} (\text{p}K_s + \log C_{\text{tr}})$$

$$\text{pH} = \text{p}K_e - \frac{1}{2} (\text{p}K_s + \log C_{\text{tr}})$$

A.N. $\text{pH}_{\text{li1}} = 6,5$

entre $\text{Zn}(\text{OH})_2(\text{csd})$ et $\text{Zn}(\text{OH})_4^{2-}$



$$\beta = \frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{OH}^-]^2} = \frac{C_{\text{tr}}}{\beta} \Rightarrow [\text{OH}^-]_{\text{ei}}^2 = \frac{C_{\text{tr}}}{\beta}$$

$$2 \log[\text{OH}^-]_{\text{ei}} = \log C_{\text{tr}} - \log \beta$$

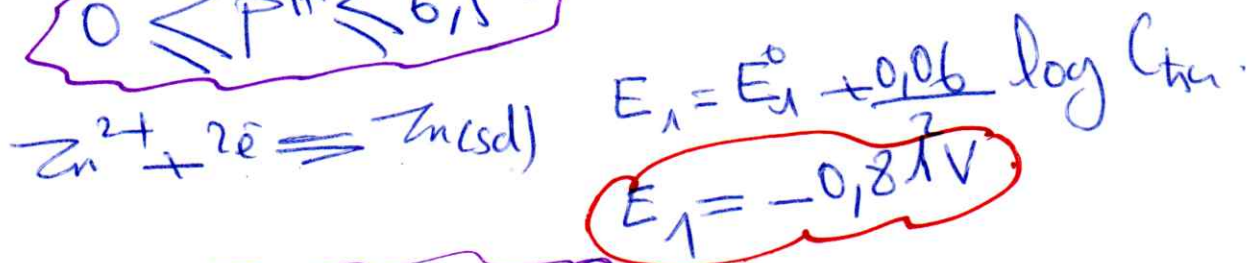
$$\text{pOH} = \frac{1}{2} (\log \beta - \log C_{\text{tr}})$$

$$\text{pH}_{\text{li2}} = \text{p}K_e - \frac{1}{2} (\log \beta - \log C_{\text{tr}})$$

$$\text{pH}_{\text{li2}} = 13,75$$

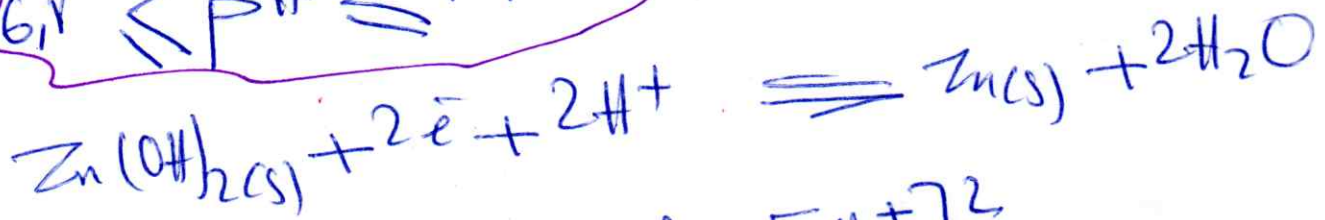
Determination $\rightarrow$ potentials $\rightarrow$ electrode.

$$0 \leq \text{pH} \leq 6,5$$



$$E_1 = -0,81 \text{ V}$$

$$6,5 \leq \text{pH} \leq 13,7$$



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

$$E_2 = E_2^0 - 0,06 \text{ pH}$$

$\text{pH} = 6,5$, then $E_1 = E_2 = -0,81$

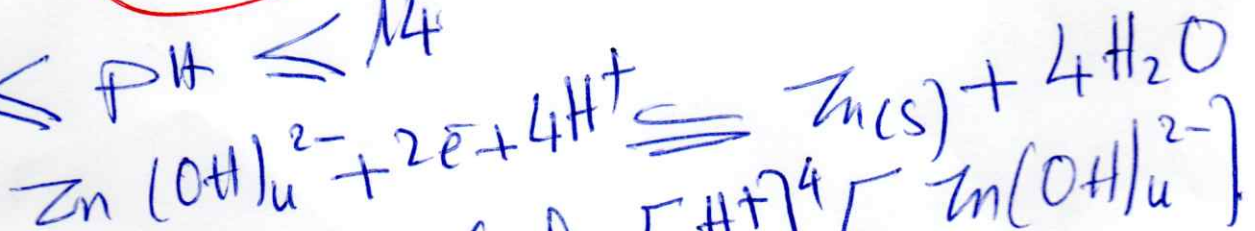
$$\Rightarrow E_2^0 = -0,81 + 0,06 \times 6,5$$

$$E_2^0 = -0,42 \text{ V}$$

$$\Rightarrow E_2 = -0,42 - 0,06 \text{ (V)} \quad \text{pH} = 13,7$$

$$E_2 = -1,24 \text{ V}$$

$$13,7 \leq \text{pH} \leq 14$$



$$E_3 = E_3^0 + \frac{0,06}{2} \log [\text{H}^+]^4 \left[\frac{\text{Zn(OH)}_4^{2-}}{C_{\text{Zn}}''} \right]$$

$$E_3 = E_3^0 + 0,03 \log 10^{-2} - 0,12 \text{ pH}$$

$$E_3 = E_3^0 - 0,06 - 0,12 \text{ pH}$$

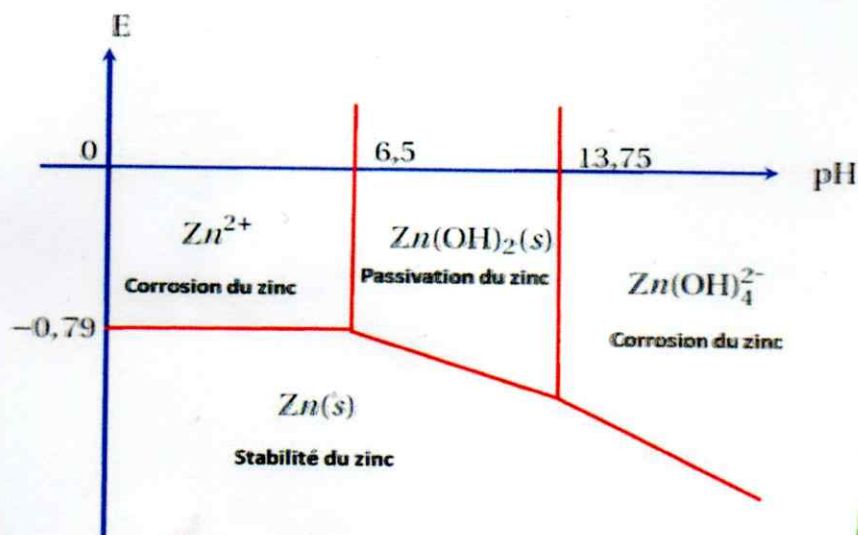
$$\text{pH} = 13,75 \quad E_2 = E_3 = -1,24 \text{ V}$$

$$E_3^0 - 0,06 - 0,12 \times 13,75 = -1,24$$

$$\rightarrow E_3^0 = 0,47$$

$$\rightarrow E_3 = 0,47 - 0,12 \text{ pH}$$

Diagramme potentiel-pH relatif au Zinc



P- 14-