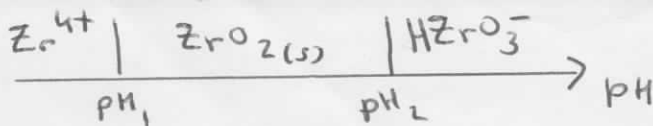


**Exo 1**

$C_0 = 10^{-6} \text{ mol.l}^{-1}$



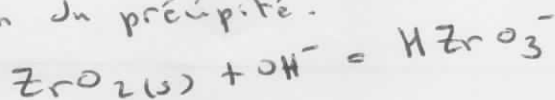
1) - apparition du précipité



$Q = [Zr^{4+}][OH^-]^4 = K_1^{-1} \qquad C_0 \frac{K_e^4}{R^4} = K_1^{-1}$

$R^4 = \frac{C_0 K_e^4}{K_1^{-1}} = \frac{10^{-6} \cdot 10^{-56}}{10^{-55,1}} = 10^{-0,9} \qquad \underline{pH_1 = 1,7}$

- disparition du précipité.



$K_2 = \frac{[HZrO_3^-]}{[OH^-]} = \frac{C_0 R}{K_e}$

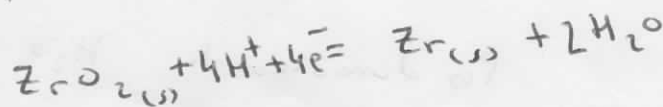
$R = \frac{K_2 K_e}{C_0} = \frac{10^{-4,8} \cdot 10^{-14}}{10^{-6}} = 10^{-12,8} \qquad \underline{pH_2 = 12,8}$

2) -  $Zr^{4+} | Zr(s) \qquad Zr^{4+} + 4e^- = Zr(s)$

$E = E^0 + \frac{0,06}{4} \log [Zr^{4+}] = E^0 + 0,015 \log C_0$

$\underline{E = -1,53V}$

-  $ZrO_2(s) | Zr(s)$



$E = E^0_{(s)} + 0,015 \log [H^+]^4$

$E = E^0_{(s)} - 0,06 \text{ pH}$

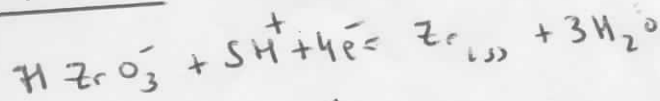
par continuité à

$pH = 1,7$

$E = -1,53 \Rightarrow E^0_{(s)} = -1,43V$

$\underline{E = -1,43 - 0,06 \text{ pH}}$

-  $HZrO_3^- | Zr(s)$



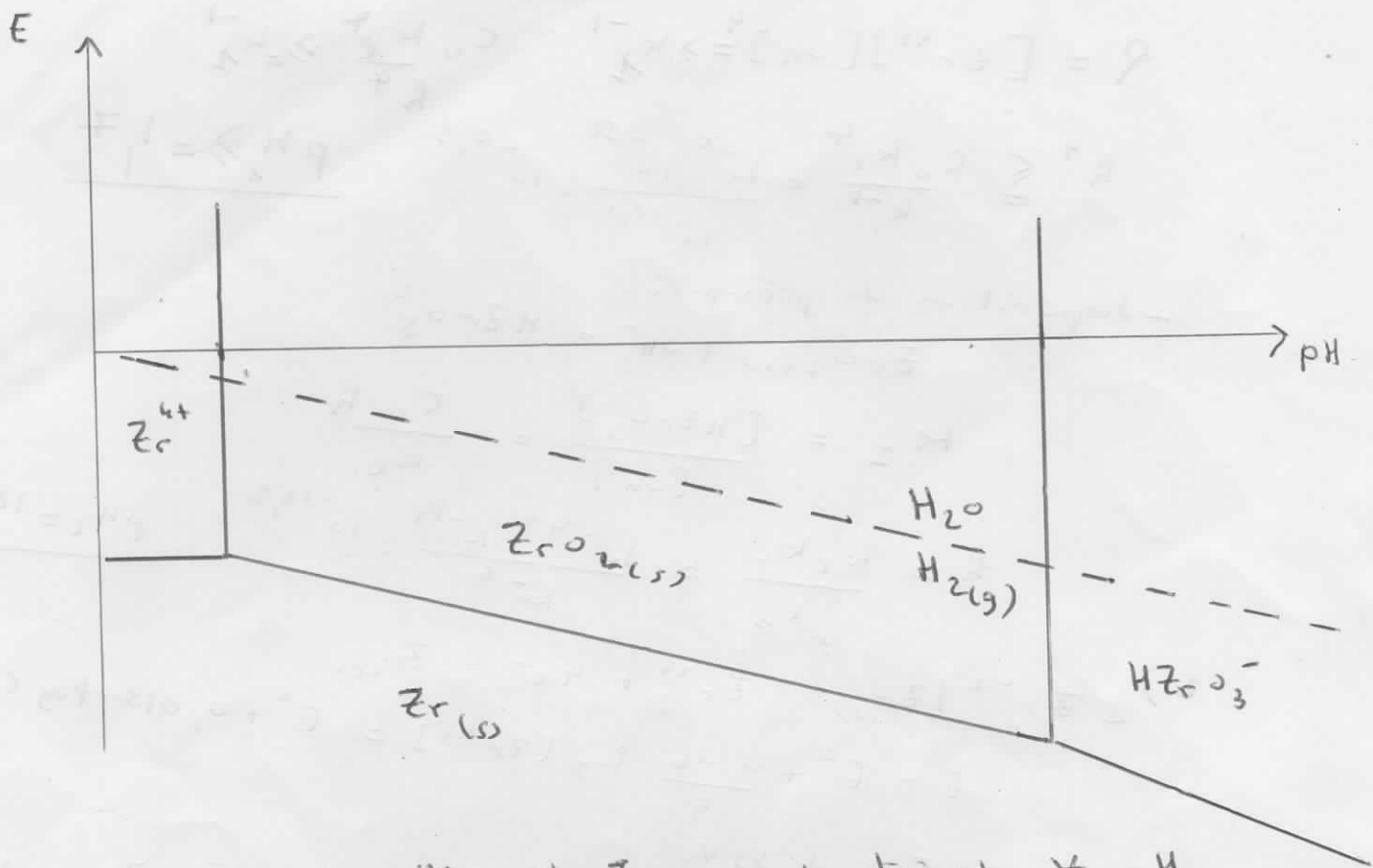
$E = E^0_{(s)} + \frac{0,06}{4} \log [H^+]^5 C_0$

$E = E^0_{(s)} + 0,015 \log C_0 - 0,075 \text{ pH}$

continuité :  $pH = 12,8 \qquad E = -2,195V$

$E^0_{(s)} + 0,015 \log C_0 = -1,23$

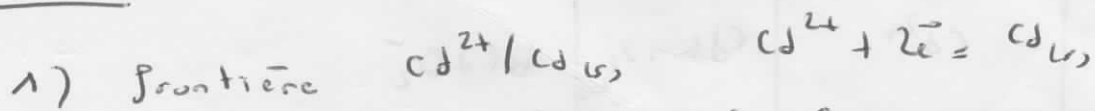
$\underline{E = -1,23 - 0,075 \text{ pH}}$



Pourbaix diagram de  $\text{H}_2\text{O}$  et  $\text{Zr(s)}$  sont joints  $\forall \text{pH}$ .

$\text{Zr(s)}$  sera oxydé dans  $\forall \text{pH}$ .

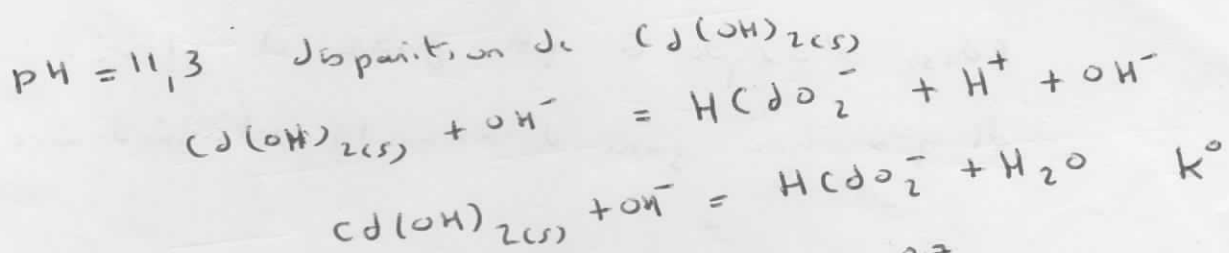
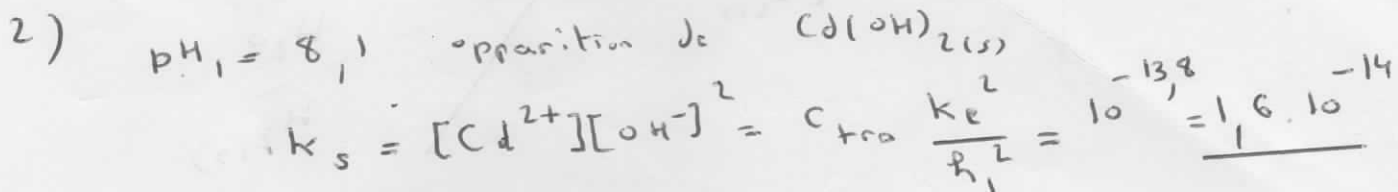
# Exo 2



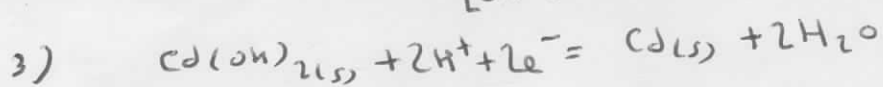
$$E = E^{\circ} + 0,03 \log C_{tra}$$

$$E^{\circ} = -0,46 - 0,03 \log 10^{-2}$$

$$\underline{E^{\circ}_{(Cd^{2+}/Cd)} = -0,4V}$$



$$K^{\circ} = \frac{[HCO_2^-]}{[OH^-]} = \frac{C_{tra}}{K_e} h_2 = 10^{0,7} = \underline{5}$$



$$E = E^{\circ}_{(\dots)} + \frac{0,05}{2} \log [H^+]^2 = E^{\circ}_{(\dots)} - 0,06 pH$$

unité du potentiel.

$$E = E^{\circ}_{(Cd^{2+}/Cd)} + \frac{0,06}{2} \log [Cd^{2+}]$$

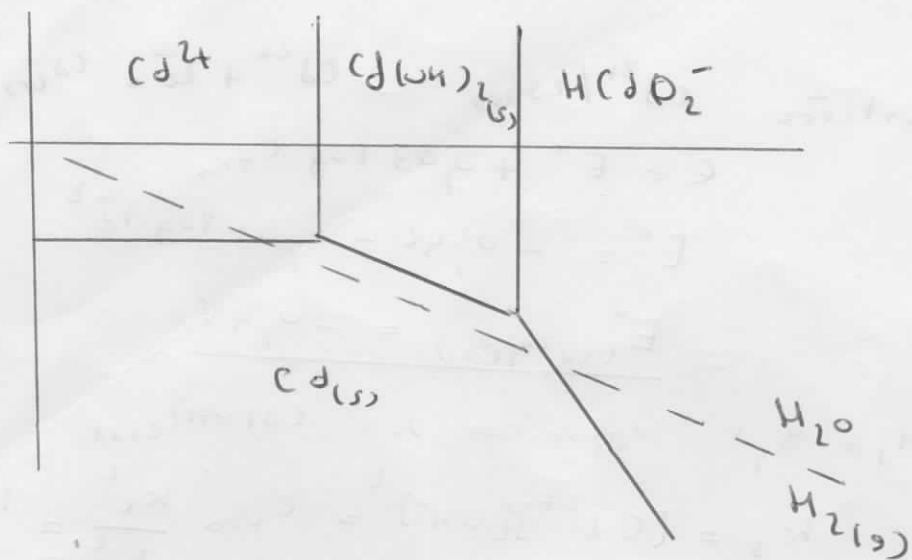
$$E = E^{\circ}_{(Cd(OH)_2/Cd)} + \frac{0,06}{2} \log [H^+]^2 = E^{\circ}_{(\dots)} + 0,06 \log \frac{K_e}{[OH^-]}$$

Sat  $E^{\circ}_{(\dots)} = E^{\circ}_{(Cd^{2+}/Cd)} + 0,03 \log \frac{[Cd^{2+}][OH^-]^2}{K_e}$

$$\begin{aligned} E^{\circ}_{(\dots)} &= E^{\circ}_{(Cd^{2+}/Cd)} - 0,03 pK_s + 0,06 pK_e \\ &= -0,4 - 0,03 \times 13,8 + 0,06 \times 14 \\ &= \underline{0,026V} \end{aligned}$$

$$E = 0,026 - 0,06 pH \approx \underline{0,03 - 0,06 pH}$$

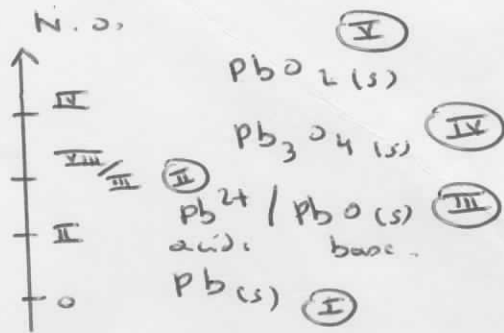
4)



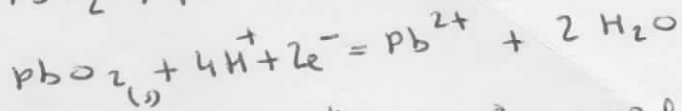
$Cd(s)$  s'oxyde à pH faible et élevé.  
 Il y a une zone d'immunité intermédiaire.

**Exo 3**

1)



2) frontière (V) | (II)



$E = E^0 + \frac{0,06}{2} \log \frac{[H^+]^4}{[Pb^{2+}]} = E^0 - 0,03 \log c_{tra} - 0,12 \text{ pH}$

à  $\text{pH} = 0$   $E = 1,45 \text{ V}$  soit

$E^0 = E + 0,03 \log c_{tra} = 1,45 \text{ V}$

$E = 1,45 - 0,12 \text{ pH}$

3) cf énoncé.

4) pH faible

$Pb(s)$ , et  $H_2O$  ont des domaines disjoint.

$Pb^{2+} / Pb$

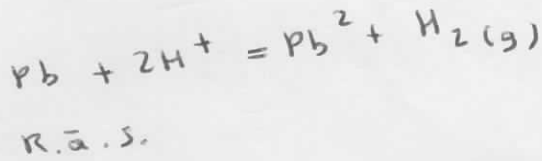
$E = E^0(Pb^{2+} / Pb) + 0,03 \log c_{tra} = -0,13 \text{ V}$

$\text{pH} = \frac{0,13}{0,06} = 2,2$

$H_2O / H_2(g)$

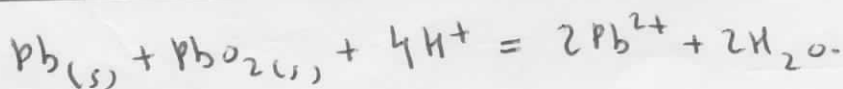
$E = -0,06 \text{ pH}$

- { si  $\text{pH} < 2,2$
- { si  $\text{pH} > 2,2$

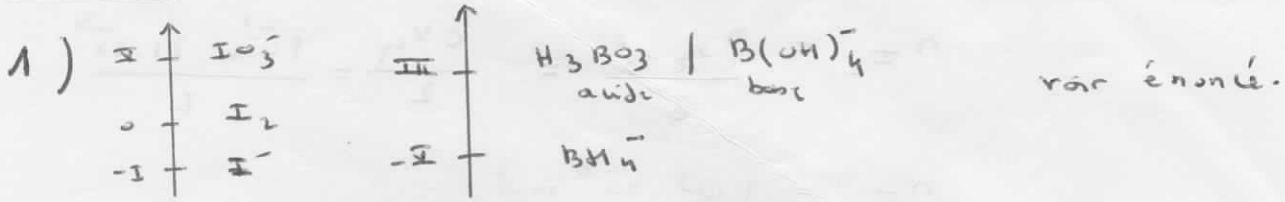


5) domaines disjoint : pas de frontières communes entre (I) et (V)

Il y a médiamutation.

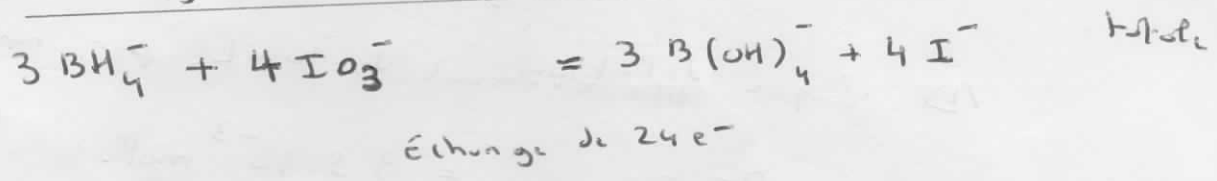
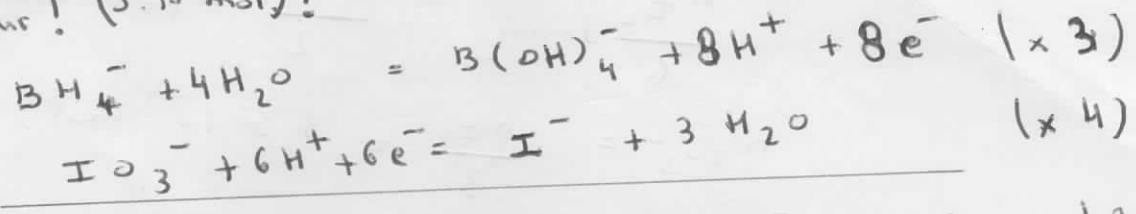


**Exo 4**

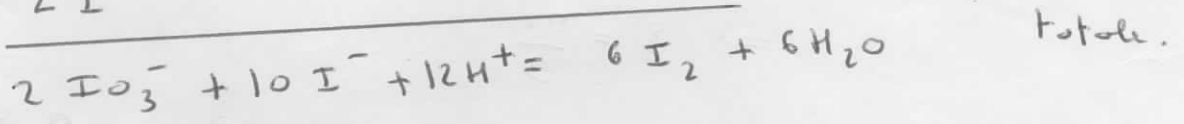
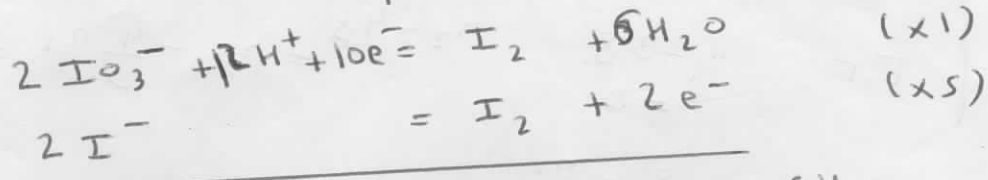


2) réaction 1 milieu basique.

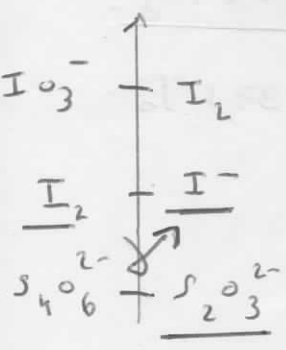
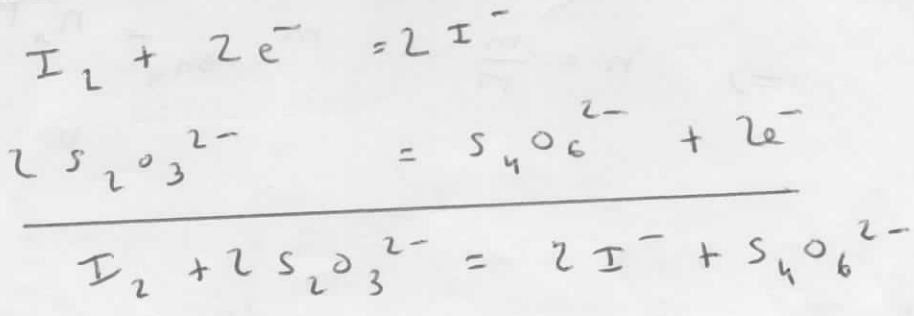
$\text{BH}_4^-$  réagit avec  $\text{IO}_3^-$  domaines adjacents  $\Rightarrow$  réaction totale.  
pas pur! ( $5 \cdot 10^{-3}$  mol)!  $10^{-2}$  mol.



réaction 2 si rate en solution  $\text{IO}_3^-$  et  $\text{I}^-$  en milieu acide, il y aura médismutation.  
le réactif limitant doit être  $\text{IO}_3^-$  ( $\Rightarrow$  excès de KI)  
pour connaître la quantité de  $\text{BH}_4^-$  ayant réagit.



réaction 3: on dose  $\text{I}_2$  formé.



3) réaction 3: équivalence.

$$n_{I_2} = \frac{n_{S_2O_3^{2-}}}{2} = \frac{cV_{eq}}{2} = \frac{10^{-1} \times 21 \cdot 10^{-3}}{2}$$

$$n_{I_2} = 1,05 \cdot 10^{-3} \text{ mol.}$$

réaction 2:  $IO_3^-$  réactif limitant.

$$\frac{n_{I_2}}{6} \text{ formé} = \frac{n_{IO_3^-} \text{ disparu}}{2}$$

$$n_{IO_3^-} = \frac{n_{I_2}}{3} = 3,5 \cdot 10^{-4} \text{ mol.}$$

1) se y a pratiquement de 10 mL par rapport à 100 mL

$$n_{IO_3^-} \text{ initial} = 3,5 \cdot 10^{-3} \text{ mol.}$$

réaction 4:  $IO_3^-$  est en excès



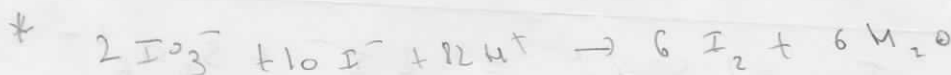
mol.	E.I	$n_1$	$n_2$	$n_1$	$\frac{4n_1}{3}$
		$n_1 - 3s$	$n_2 - 4s$	$n_2 - \frac{4}{3}n_1$	$3,5 \cdot 10^{-3}$
	E.F	$= 0$			

$$\Rightarrow s = \frac{n_1}{3}$$

$$10^{-2} - \frac{4}{3}n_1 = 3,5 \cdot 10^{-3} \quad n_1 = n_{BH_4^-} = 4,875 \cdot 10^{-3} \text{ mol.}$$

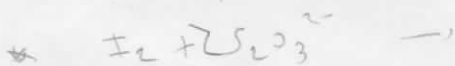
$$\Rightarrow n = \frac{m}{M} \quad m_{NaBH_4} = n_1 M = 0,184 \text{ g.}$$

pureté 97,5%



$$\frac{n_2 - \frac{4n_1}{3}}{10} - 2s = 0 \quad \text{avec } s = \frac{4n_1}{30}$$

$$C.F. = \frac{3n_2 - 4n_1}{10}$$



$$\frac{3n_2 - 4n_1}{10} \text{ éq.}$$

$$\frac{3n_2 - 4n_1}{10} = \frac{cV_{eq}}{2}$$