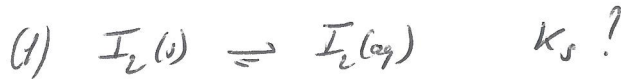
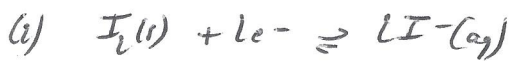


TD oxydo-reduct et Thermodynamie - EpH

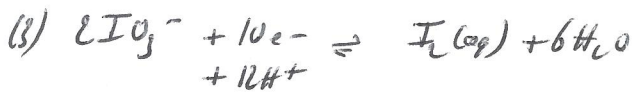
Exercice 8:



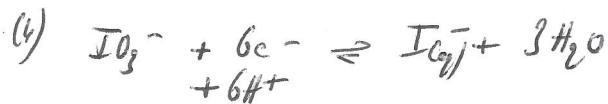
$\Delta_r G_1^0 = -RT \ln K_s$



$\Delta_r G_2^0 = -2FE_2^0$



$\Delta_r G_3^0 = -10FE_3^0$



$\Delta_r G_4^0 = -6FE_4^0$

(1) = (2) - 2(4) + (3) $\Delta_r G_1^0 = \Delta_r G_2^0 - 2\Delta_r G_4^0 + \Delta_r G_3^0$

$-RT \ln K_s = -2FE_2^0 + 12FE_4^0 - 10FE_3^0$

$- \log K_s = \frac{12E_4^0 - 2E_2^0 - 10E_3^0}{0,06} = 4$

$K_s = 10^{-4}$
 $s = 10^{-4} \text{ mol.L}^{-1}$

A saturation $K_s = s = 10^{-4}$

Exercice 9:

II	Ca^{4+}	$Ca(OH)_2(s)$
IV	Ca^{2+}	$Ca(OH)_2(s)$
0	Ca	

A la limite d'app de $Ca(OH)_2(s)$

$K_{s1} = 10^{-21} = [Ca^{4+}] \omega^2$
 $[Ca^{4+}] = c_{tra} = 10^{-2} \text{ mol.L}^{-1}$

$\omega = 10^{-\frac{19}{2}} = 10^{-6,3}$
 $pH = 7,7$

A la limite d'app de $Ca(OH)_2(l)$

$K_{s2} = 10^{-50} = [Ca^{4+}] \omega^4$
 $[Ca^{4+}] = c_{tra} = 10^{-2} \text{ mol.L}^{-1}$

$\omega = 10^{-\frac{48}{4}} = 10^{-12}$
 $pH = 2$

III/0:

$pH \leq 7,7$
 $pH \geq 7,7$

$E_1 = E_{Ca^{4+}/Ca}^0 + 0,02 \log c_{tra} = -2,37V$
 $E_2 = E_{Ca^{4+}/Ca}^0 + 0,02 \log \frac{K_{s1}}{\omega^2} = c_{te} - 0,06pH$

$\alpha_{pH=7,7} - 2,37 = c_{te} - 0,06pH$
 $c_{te} = -1,91V$

II/III

$pH \leq 2$
 $2 \leq pH \leq 7,7$

$E_3 = E_{Ca^{4+}/Ca^{2+}}^0 = 1,74V$
 $E_4 = E_{Ca^{4+}/Ca^{2+}}^0 + 0,06 \log \frac{K_{s2}/\omega^4}{c_{tra}} = c_{te}' - 0,24pH$

$\alpha_{pH=2} 1,74 = c_{te}' - 0,24pH$
 $c_{te}' = 2,22V$

Y-a-t-il un intervalle avec

E_1 au $pH = 7,7$, NoN car $E_4(7,7) = 0,37V > E_1$

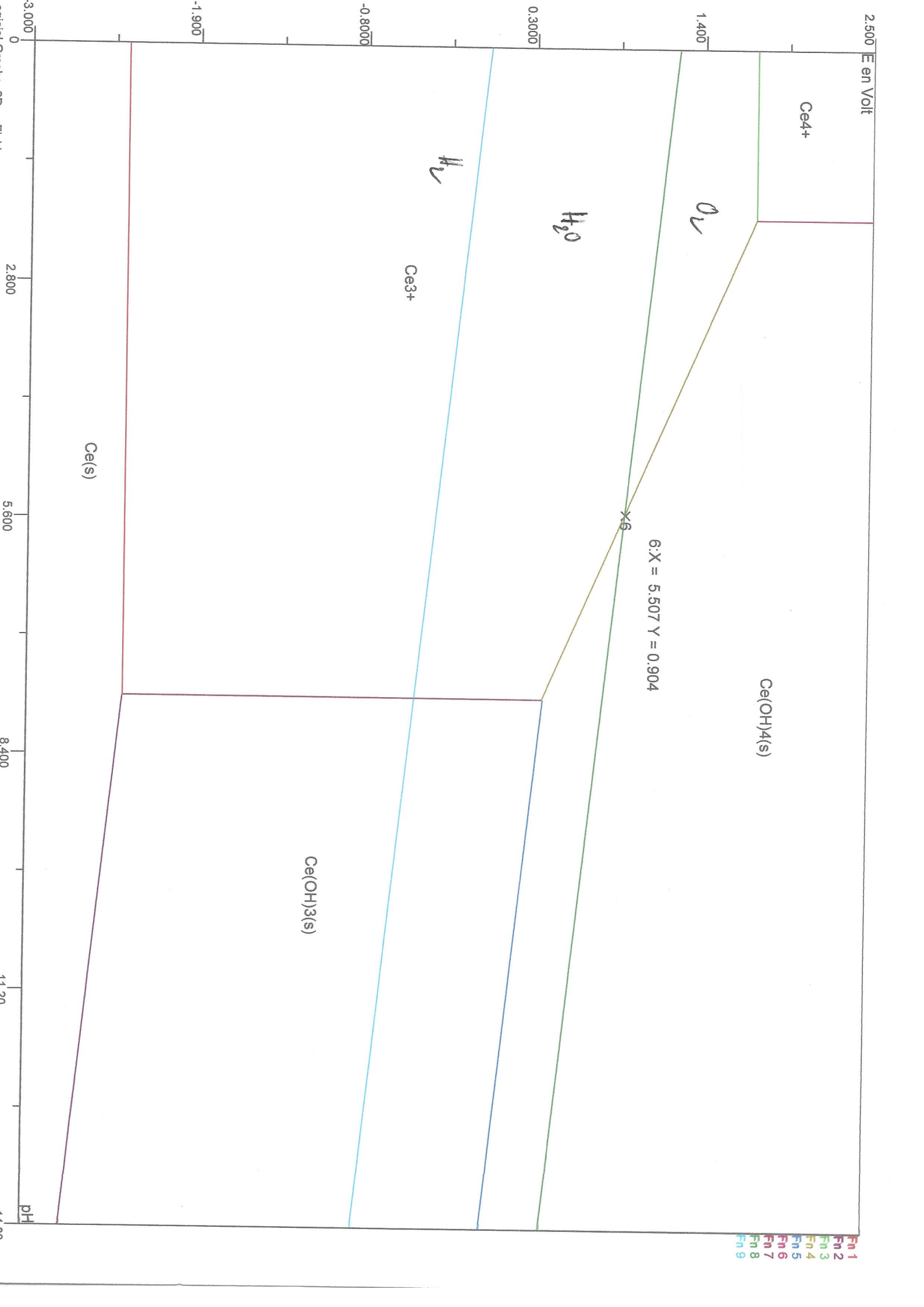
$pH \geq 7,7$

$E_5 = E_{Ca^{4+}/Ca^{2+}}^0 + 0,06 \log \frac{K_{s1}/\omega^2}{K_{s1}/\omega^2} = c_{te}'' - 0,06pH$

$\alpha_{pH=7,7} c_{te}' - 0,24pH = c_{te}'' - 0,06pH$
 $c_{te}'' = 0,84V$

Deg EpH car:

$O_2/H_2O \quad 1,23 - 0,06pH$ $H_2O/H_2 \quad -0,06pH \Rightarrow$ III stable $\forall pH$
 IV stable si $pH > 5,5$

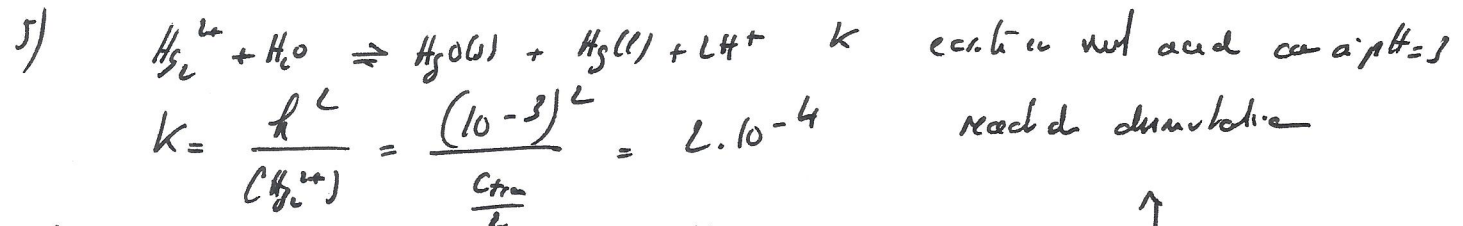
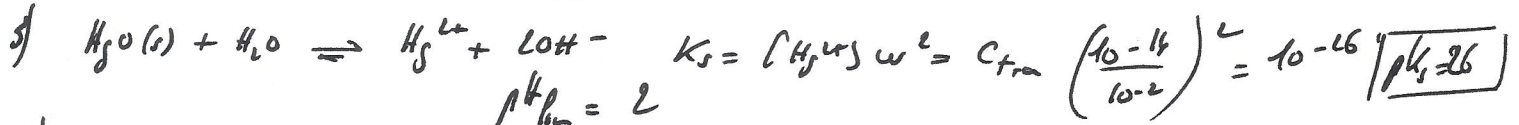


Exercice 11

1) tab. préférentiel

+II	(A) Hg^{2+}	(D) $HgO(s)$
+I	Hg_2^{2+} (B)	
0	$Hg(l)$ (C)	

- 2) E_1^0 ! A la frontière $0,85 = E_1^0 + 0,03 \log \frac{[Hg^{2+}]^L}{[Hg_2^{2+}]^L}$ et $[Hg^{2+}] = \frac{C_{tra}}{L}$ $[Hg_2^{2+}] = \frac{C_{tra}}{4}$
 $E_1^0 = 0,85 - 0,03 \log C_{tra} \Rightarrow |E_1^0 = 0,91V|$
 E_2^0 ! A la frontière $0,73 = E_2^0 + 0,03 \log [Hg_2^{2+}]$ et $[Hg_2^{2+}] = \frac{C_{tra}}{L} = 5 \cdot 10^{-2} mol/l$
 $E_2^0 = 0,73 - 0,03 \log \frac{C_{tra}}{L} = |0,90V = E_2^0|$



- 6) a) Non car dans l'eau avec H_2O à pH
 b) Non.
 c) Hg et Hg_2^{2+} oxydés par O_2

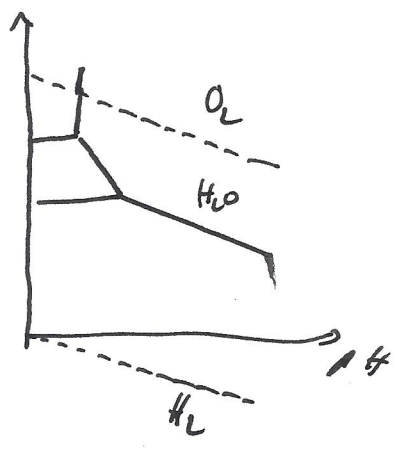


Diagramme potential-pI de l'element mesure

E.12

1) $Hg^{2+} \rightleftharpoons Hg^{2+} + Hg(l) \quad K_d \quad \text{soit}$ $\log K_d = \frac{1}{0,06} (E_{Hg^{2+}/Hg}^0 - E_{Hg^{2+}/Hg^{2+}}^0)$
 At'quilibre $E_{Hg^{2+}/Hg^{2+}} = E_{Hg^{2+}/Hg}$ $\log K_d = -1,8$
 Pour une valeur de Hg^{2+} et stable en solution

2) (a) $Hg^{2+} + 2e^- \rightleftharpoons Hg(l) \quad E = E_3^0 + 0,03 \log [Hg^{2+}] \quad (iii)$

(b) $Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l) \quad E = E_2^0 + 0,03 \log [Hg_2^{2+}] \quad (ii)$

(c) $2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+} \quad E = E_1^0 + 0,03 \log \frac{[Hg^{2+}]^2}{[Hg_2^{2+}]} \quad (i)$

2(ii) - (i) = (iii) : $2E - E - E = 2E_3^0 - E_1^0 - E_2^0$

$E_3^0 = \frac{E_1^0 + E_2^0}{2} = 0,855 V$

3) a) $\begin{cases} K_s = [Hg_2^{2+}][I^-]^2 \\ [Hg_2^{2+}] = 10^{-2} \text{ mol} \cdot L^{-1} \end{cases} \quad [I^-] = \sqrt{\frac{10^{-2}}{10^{-2}}} = 10^{-13} \text{ mol} \cdot L^{-1} \quad \rho I = 13$

b) $\rho I = \frac{\log K_{sp}}{4} = 7,5$

c) Table préférentiel:

II	$Hg_2I_4^{2-}$	7,5	Hg^{2+}
I	$Hg_2I_2(l)$		Hg_2^{2+}
0	$Hg(l)$	13	

ρI

d) $\underline{0 \text{ II / I}} \quad | \rho I \geq 13 | \quad Hg^{2+}/Hg_2^{2+} \quad E = E_1^0 + 0,03 \log c_{tra} = 0,85 V$

$\underline{13 \geq \rho I \geq 7,5} \quad Hg^{2+}/Hg_2I_2(l) \quad 2Hg^{2+} + 2e^- + 2I^- \rightleftharpoons Hg_2I_2(l)$

$E = E_{Hg^{2+}/Hg_2I_2}^0 + 0,03 \log [Hg^{2+}]^2 [I^-]^2 = \alpha - 0,06 \rho I = 1,63 - 0,06 \rho I$

Calculer à $\rho I = 13 \quad 0,85 = \alpha - 0,06 \times 13 \Rightarrow \alpha = 1,63 V$

$\underline{|\rho I \leq 7,5|} \quad 2Hg_2I_4^{2-} + 2e^- \rightleftharpoons Hg_2I_2(l) + 6I^- \quad E = \alpha' + 0,18 \rho I = -0,17 + 0,18 \rho I$

Calculer à $\rho I = 7,5 \quad 1,63 - 0,06 \times 7,5 = \alpha' + 0,18 \times 7,5 \quad \alpha' = -0,17 V$

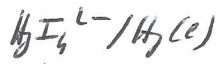
$\bullet \underline{I / 0} \quad | \rho I \geq 13 | \quad E = E_2^0 + 0,03 \log c_{tra} = 0,74 V$

$\underline{|\rho I \leq 13|} \quad Hg_2I_2 + 2e^- \rightleftharpoons Hg(l) + 2I^- \quad E = \alpha'' + 0,06 \rho I = -0,04 + 0,06 \rho I$

par calculer à $\rho I = 13 \quad 0,74 = \alpha'' + 0,06 \times 13 \quad \alpha'' = -0,04 V$

$\bullet \underline{\text{intermed}}: \text{II / I et I / 0} \quad \text{pour } \rho I \leq 7,5 ? \quad -0,17 + 0,18 \rho I = -0,04 + 0,06 \rho I$
 $\rho I = 1,08$

Pour $\rho I \leq 1,08$

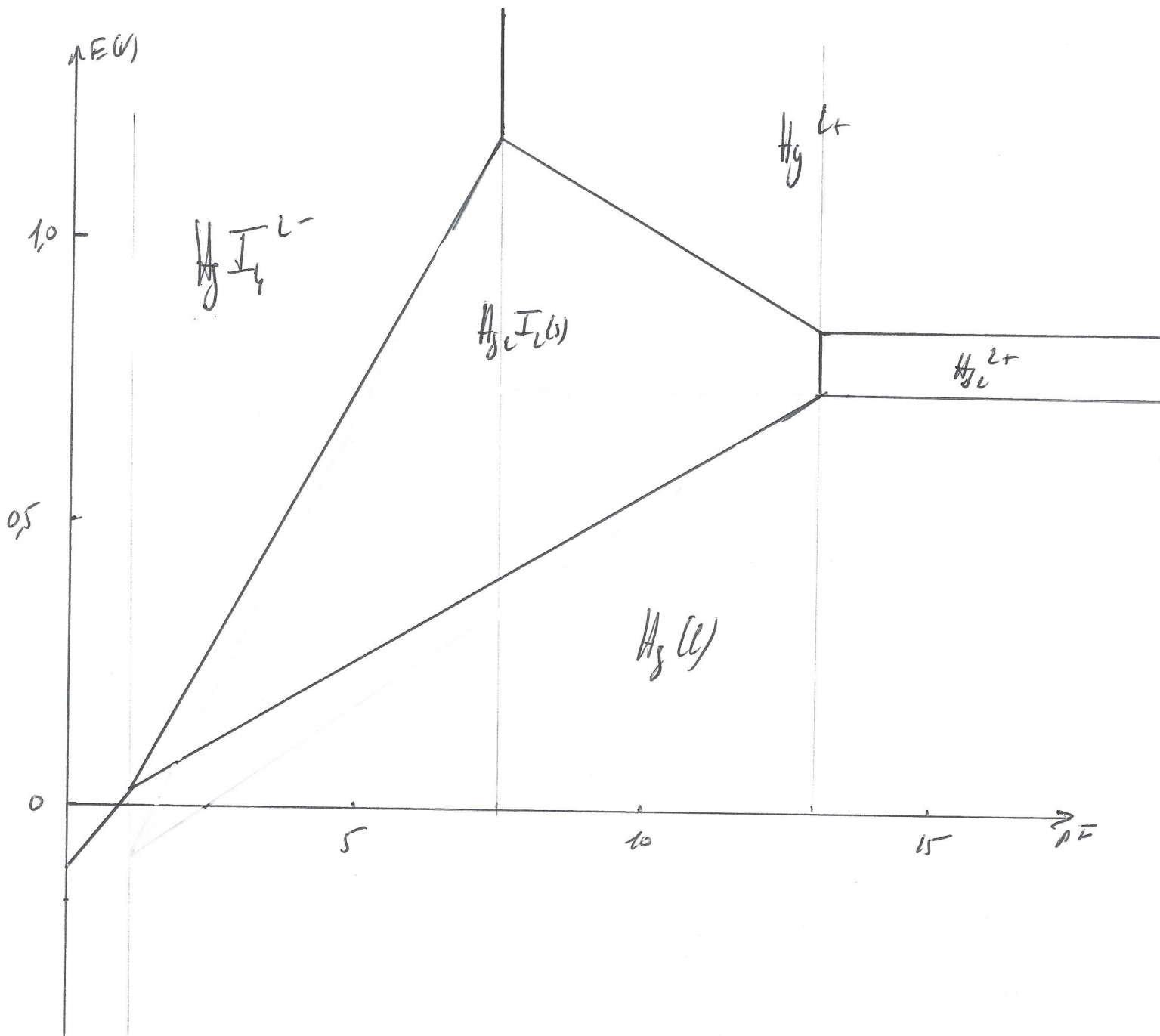


$E = \alpha'' + 0,12\rho I \approx -0,11 + 0,12\rho I$

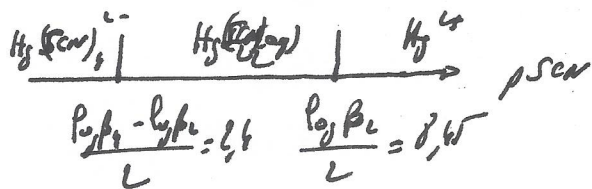
Pour $\rho I > 1,08$

$\alpha'' + 0,12 \times 1,08 = -0,04 + 0,06 \times 1,08$

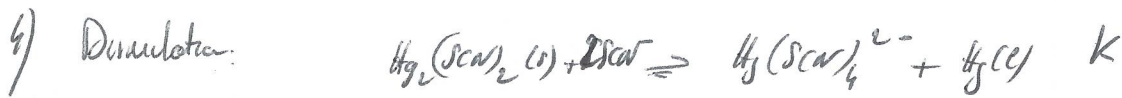
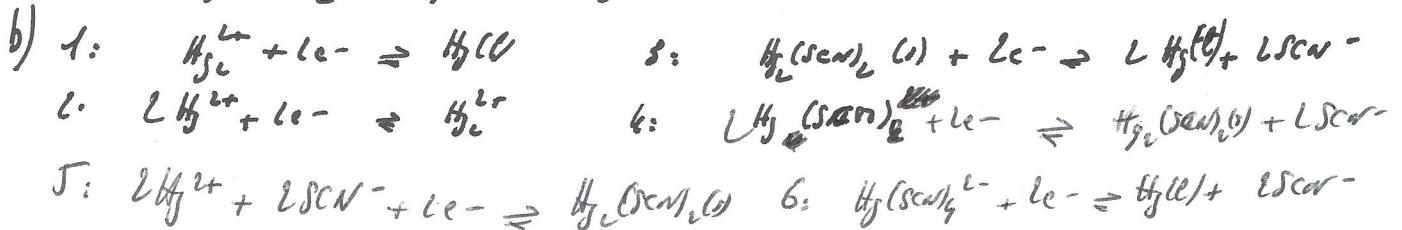
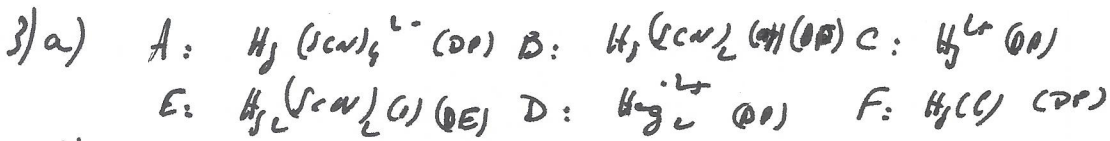
$\alpha'' = -0,11 V$



TD deux, E_p et E_{pL}
 Exercice 43: 1)



1) $\frac{\text{H}_2(\text{SCN})_2 \rightleftharpoons \text{H}_2^{\ominus} \rightarrow p_{\text{SCN}}}{\frac{1}{L} p_{\text{H}_2} = 9,85}$ Alalut $K_1 = \frac{[\text{H}_2^{\ominus}][\text{SCN}^-]}{[\text{H}_2(\text{SCN})_2]}$
 $p_{\text{SCN}} = \frac{1}{L} p_{K_1} - \frac{p_{\text{H}_2}}{L}$



$$K = \frac{[\text{H}_2(\text{SCN})_2^{\ominus}]}{[\text{SCN}^-]^2} = \frac{c_{\text{tra}}}{(10 - p_{\text{SCN}})^2} \quad \text{or } p_{\text{SCN}} = 0$$

E^{\ominus} $\Rightarrow c_{\text{tra}} = 1 \text{ mol.l}^{-1} \quad \Rightarrow \underline{\underline{K = 1}}$

a) la depot et des e la dissolch

Alalut

$$1 = \frac{c[\text{H}_2(\text{SCN})_2^{\ominus}]}{[\text{SCN}^-]^2}$$

$c[\text{H}_2(\text{SCN})_2^{\ominus}] = 0,1 \text{ mol.l}^{-1}$

$\Rightarrow [\text{SCN}^-] = \sqrt{10^{-1}}$

$n_{\text{SCN}^-} = (\text{SCN}^-) V + 2 \times 0,1 \times V = \dots$
 \uparrow
 $[\text{H}_2(\text{SCN})_2^{\ominus}]$

$\approx 0,90 \text{ V}$

TD Cinétique

PCSI

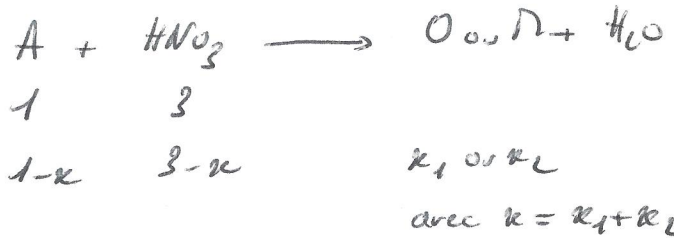
Exercice 10



et M:



$$\left\{ \begin{aligned} -\frac{d[A]}{dt} &= v_1 + v_2 \\ \frac{d[O]}{dt} &= v_1 \\ \frac{d[M]}{dt} &= v_2 \end{aligned} \right.$$



• $\frac{d[M]}{d[O]} = \frac{v_2}{v_1} = \frac{k_2 [A][HNO_3]}{k_1 [A][HNO_3]} = \frac{k_2}{k_1}$

$d[M] = \frac{k_2}{k_1} d[O]$; on intègre entre l'état initial et l'état final choisis à 1200s

$$\int_0^{[M]} d[M] = \frac{k_2}{k_1} \int_0^{[O]} d[O] \quad [M] = \frac{k_2}{k_1} [O]$$

$$\frac{k_2}{k_1} = \frac{[M]}{[O]} = 9$$

• $-\frac{d[A]}{dt} = (k_1 + k_2) [A][HNO_3]$ soit $\frac{dx}{dt} = (k_1 + k_2) (1-x)(3-x)$

$$\frac{dx}{(1-x)(3-x)} = (k_1 + k_2) dt$$

Rien: décomposé en écart simple de la forme rationnelle

$$\frac{1}{(1-x)(3-x)} = \frac{A}{1-x} + \frac{B}{3-x}$$

soit $1 = A(3-x) + B(1-x)$

pour $x=3$ $B = -\frac{1}{2}$ et pour $x=1$ $A = \frac{1}{2}$

donc on doit intégrer l'eq avec variable séparable:

$$\frac{1}{1-x} dx - \frac{1}{3-x} dx = 2(k_1 + k_2) dt$$

$$-\ln\left(\frac{1-x}{1}\right) + \ln\left(\frac{3-x}{3}\right) = 2(k_1 + k_2)t$$

à $t=1200s$, $x = 0,52$ mol donc

$$k_1 + k_2 = \frac{-\ln\left(\frac{0,48}{1}\right) + \ln\left(\frac{2,48}{3}\right)}{2t}$$

$$\left\{ \begin{aligned} (k_1 + k_2) &= 2,27 \cdot 10^{-3} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1} \\ \frac{k_2}{k_1} &= 9 \end{aligned} \right.$$

$$\Rightarrow \left\{ \begin{aligned} k_1 &= 2,27 \cdot 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1} \\ k_2 &= 2,04 \cdot 10^{-4} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1} \end{aligned} \right.$$