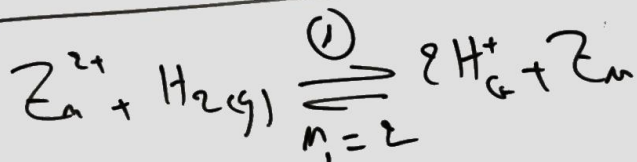
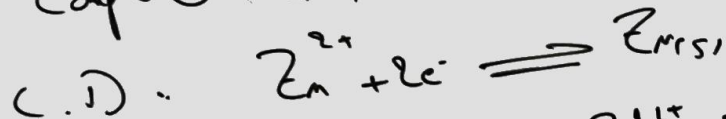


Application (1):

Exprimer $E^\circ_2(\text{Zn(OH)}_2/\text{Zn})$ en fonction

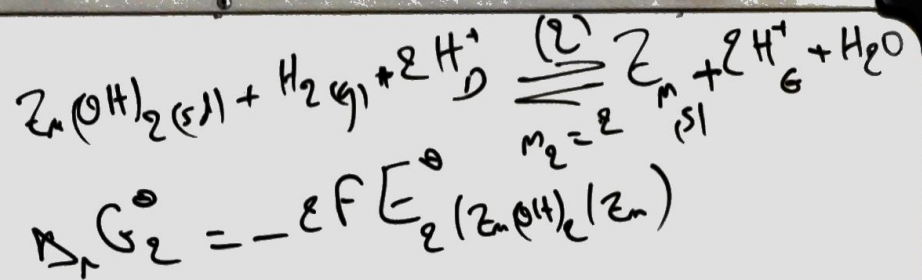
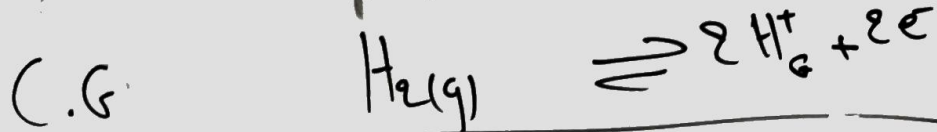
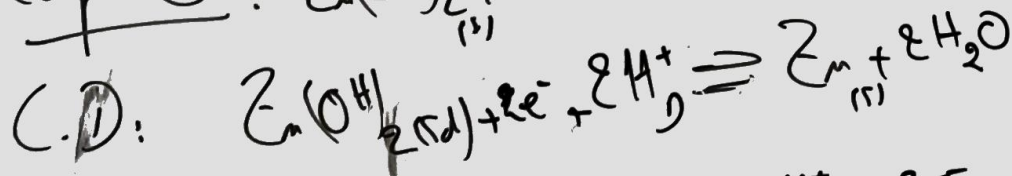
$E^\circ_1(\text{Zn}^{2+}/\text{Zn})$; $K_s(\text{Zn(OH)}_2)$ et K_e

Couple (1): $\text{Zn}^{2+}/\text{Zn(s)}$



$$\Delta_r G^\circ_1 = -2F E^\circ_1(\text{Zn}^{2+}/\text{Zn})$$

Couple (2): $\text{Zn(OH)}_2/\text{Zn(s)}$



$$\Delta_r G^\circ_2 = -2F E^\circ_2(\text{Zn(OH)}_2/\text{Zn})$$



$$\Delta_r G^\circ_3 = -RT \ln K_s$$



$$\Delta_r G^\circ_4 = -RT \ln K_e$$

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

$$\Delta_r G^\circ_2 = \Delta_r G^\circ_1 + \Delta_r G^\circ_3 - 2\Delta_r G^\circ_4$$

$$\frac{RT}{F} \ln K_x = 0.06 \log x$$

(2)

$$-2F E_2 (Zn(OH)_2 / Zn) = -2F E_1 (Zn^{2+} / Zn) - RT \ln K_s + RT \ln K_e^2$$

$$-2F E_2 = -2F E_1 + RT \ln \frac{K_e^2}{K_s}$$

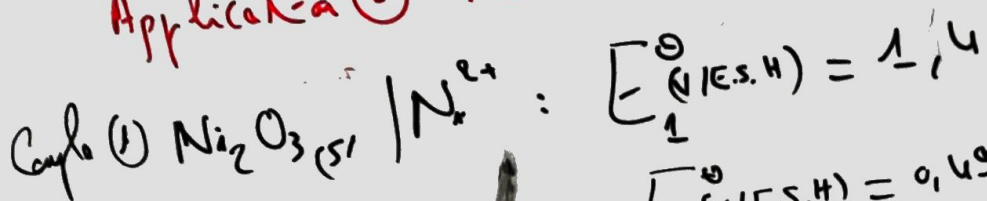
$$E_2^0 = E_1^0 - \frac{RT}{2F} \ln \frac{K_e^2}{K_s}$$

$$E_2^0 (Zn(OH)_2 / Zn) = E_1^0 (Zn^{2+} / Zn) + 0,03 \log \frac{K_s}{K_e^2}$$

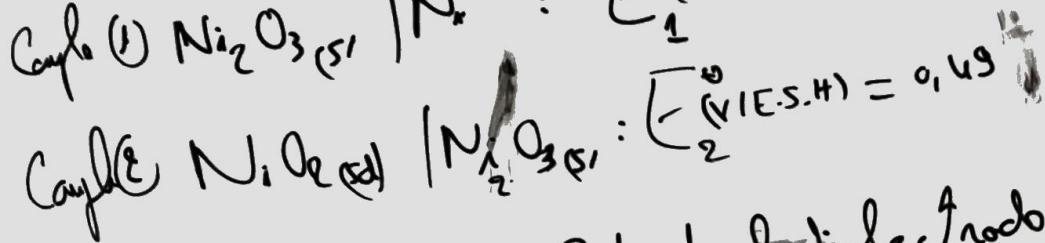
$E_3^0 (Zn(OH)_4^{2-} / Zn)$ einfach:

$$E_{Zn^{2+}/Zn}^0; K_c (Zn(OH)_4^{2-}) \text{ u. } K_e$$

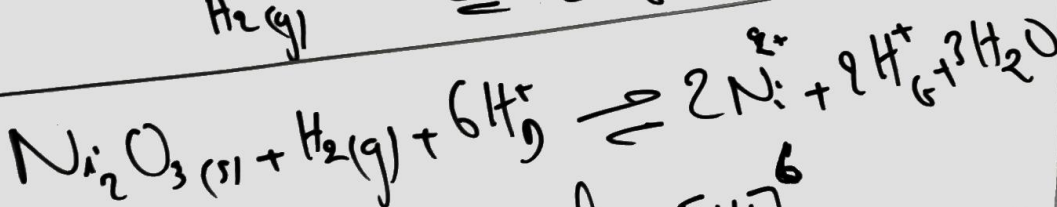
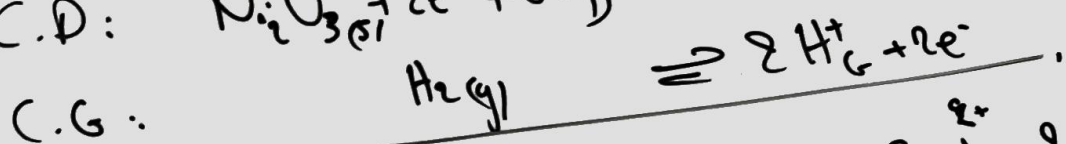
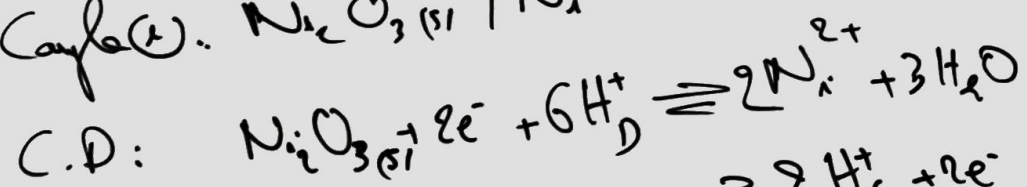
Application ② Réaction de dismutation



$$C_{\text{TNG}} = 1 \text{ M}$$



1/ Expression du Potentiel d'électrode des couples ① et ②



$$E_{(\text{NIE.S.H})} = E_1 + \frac{0,06}{2} \log \frac{[\text{H}^+]^6}{[\text{Ni}^{2+}]^2}$$

Augment D..

$$E_1(p^{\text{HD}}) = E_2(p^{\text{HD}})$$

$$1,4 - 0,18 p^{\text{HD}} = 0,49 - 0,06 p^{\text{HD}}$$

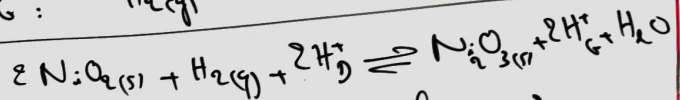
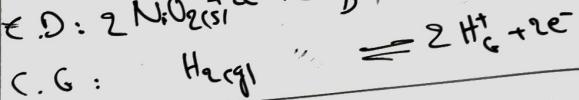
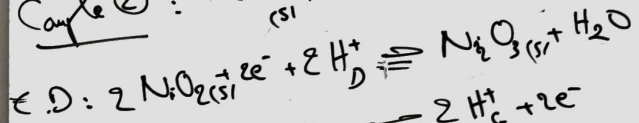
$$p^{\text{HD}} = \frac{1,4 - 0,49}{0,18 - 0,06}$$

$$p^{\text{HD}} = 7,6$$

Convention sur le diagramme ①: $[Ni^{2+}] = C_{Ni} = 10^{-1}$

$$E_{(NIE.S.H)} = 1,4 - 0,18 pH$$

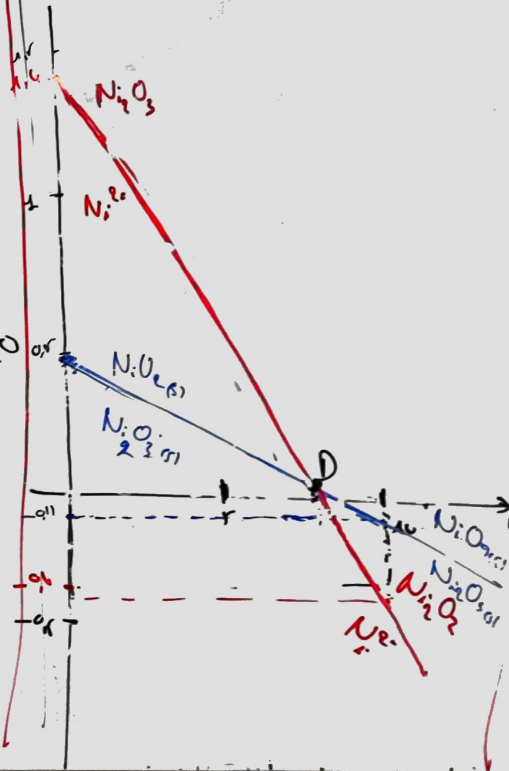
Case ②: $NiO_2(s) / Ni_2O_3(s)$



$$E_{(NIE.S.H)} = E_{(NIE.S.H)}^\circ + \frac{0,06}{2} \log [H^+]^2$$

$$E_{(NiO_2/Ni_2O_3)} = 0,49 - 0,06 pH$$

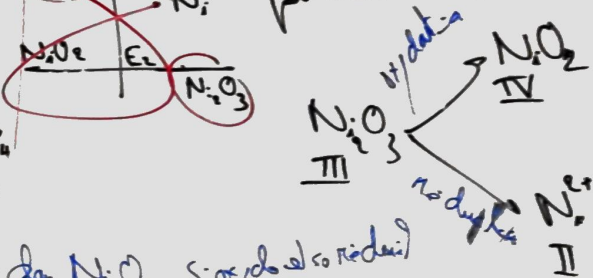
2/ Traçage de la frontière



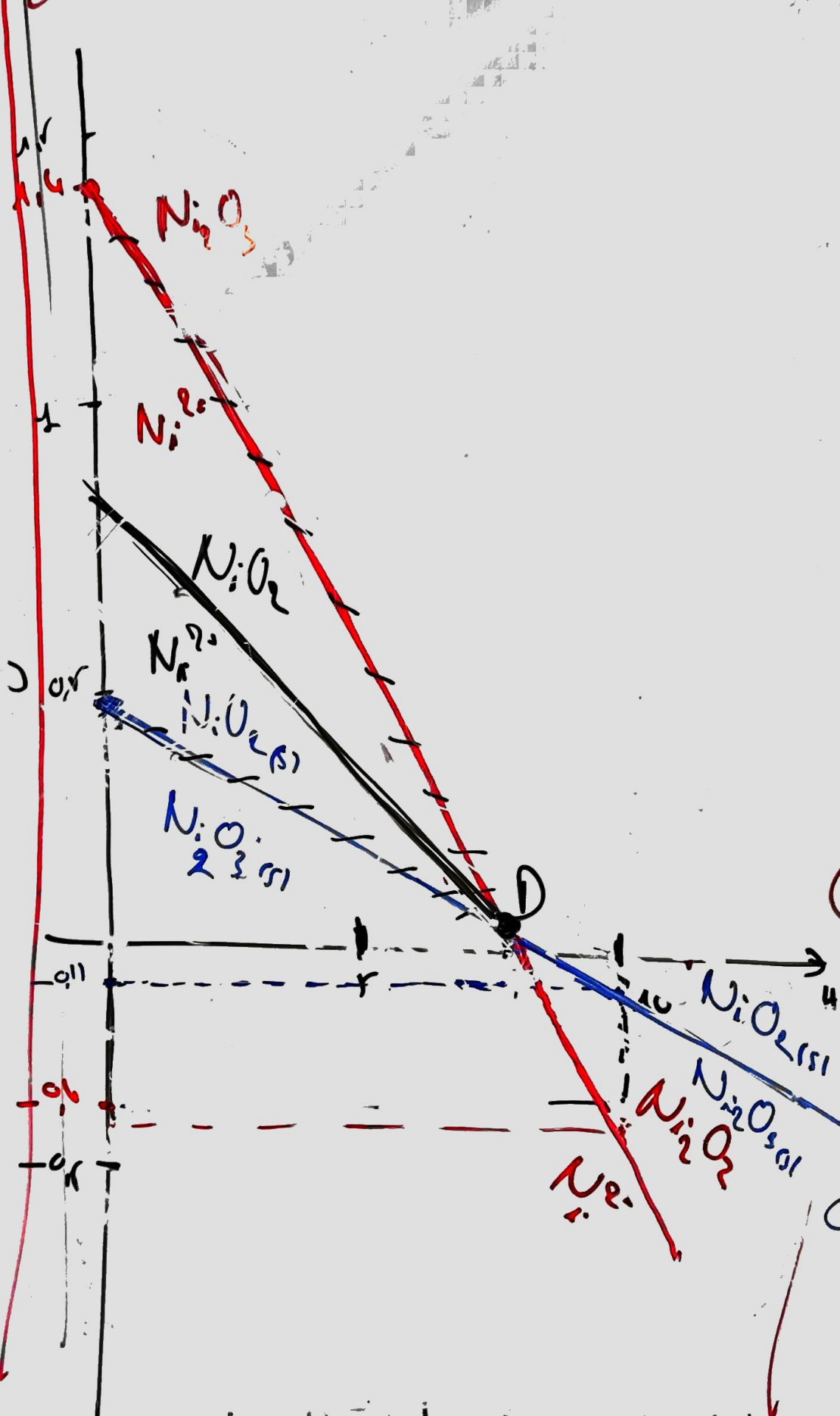
$$pH < p^H_0 = 7,6$$

* $Ni_2O_3(s) \in$ à deux domaines disjoints de NiO_2 , stable de $Ni_2O_3(s)$ réagit totalement pour donner $NiO_2(s)$ et Ni^{2+}
 $\Rightarrow Ni_2O_3$ se dissout pour donner Ni^{2+} et NiO_2

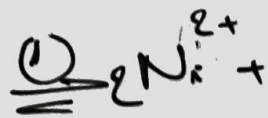
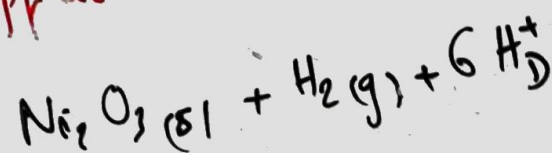
* Ni_2O_3 se comporte comme (ox) par (Red) par la Ni_2O_3 réagit totalement pour donner Ni^{2+} et NiO_2 :



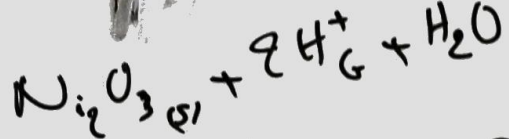
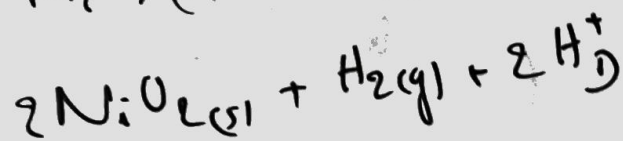
La $Ni_2O_3(s)$ s'oxyde et se réduit simultanément pour donner $NiO_2(s)$ et Ni^{2+}



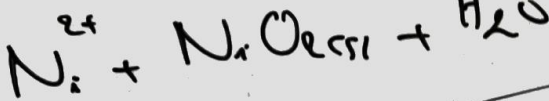
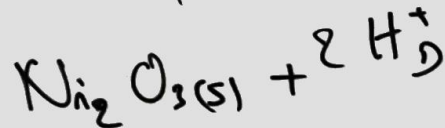
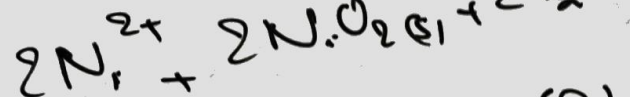
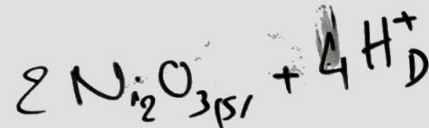
Application (2) Réaction de dissolution



$$\Delta_r G_1^\circ = -2FE_1^\circ$$



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



$$(R) = \frac{1}{2} ((1) - (2))$$

$$\Delta_r G^\circ = \frac{1}{2} (\Delta_r G_1^\circ - \Delta_r G_2^\circ)$$

$$-RT \ln K_D^\circ = \frac{1}{2} (-2FE_1^\circ + 2FE_2^\circ)$$

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

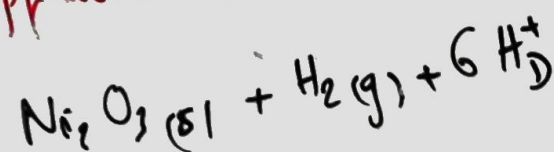
$$0.06 \log K_D^\circ = (E_1^\circ - E_2^\circ)$$

$$K_D^\circ(298) = 10^{\frac{E_1^\circ - E_2^\circ}{0.06}}$$

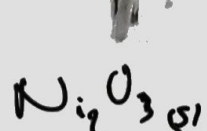
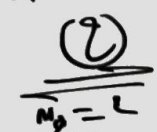
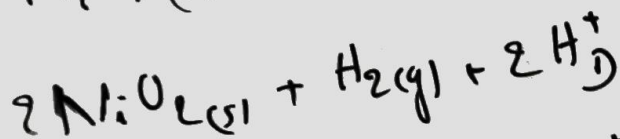
Argument: D

$$K_D^\circ = \frac{[\text{Ni}^{2+}]}{[\text{H}^+]^2} = \frac{C_{\text{Ni}}}{(10^{-\text{pH}})^2}$$

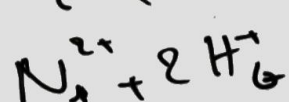
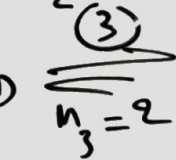
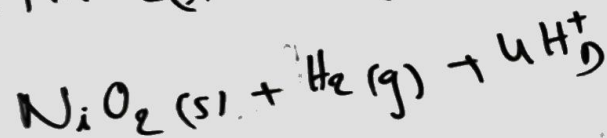
Application (2) Réaction de dismutation



$$\Delta_r G_1^\circ = -2FE_1^\circ$$



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



$$\Delta_r G_3^\circ = -2FE_3^\circ$$

$$(3) = \frac{1}{2} ((1) + (2))$$

$$\Delta_r G_3^\circ = \frac{1}{2} (\Delta_r G_1^\circ + \Delta_r G_2^\circ)$$

$$-2FE_3^\circ = \frac{1}{2} (-2FE_1^\circ - 2FE_2^\circ)$$

$$E_3^\circ = \frac{E_1^\circ + E_2^\circ}{2}$$

