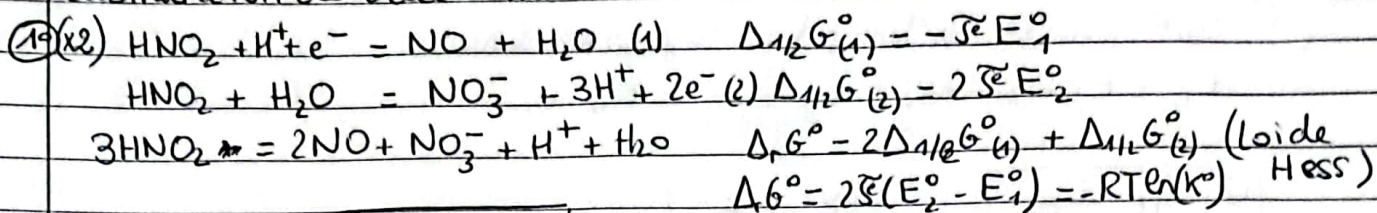
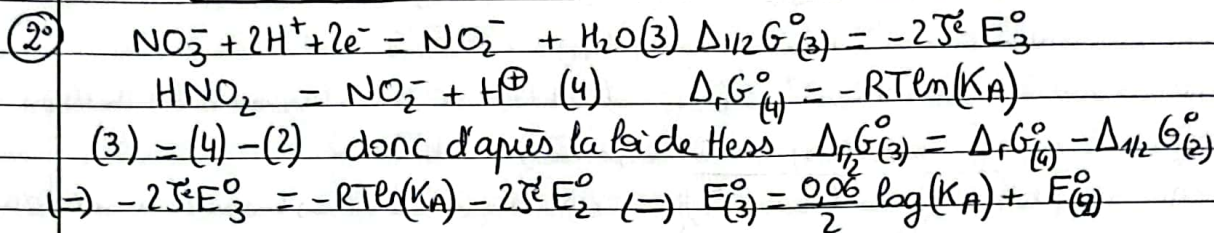


# correction TD Thermodynamique oxydo-réduction

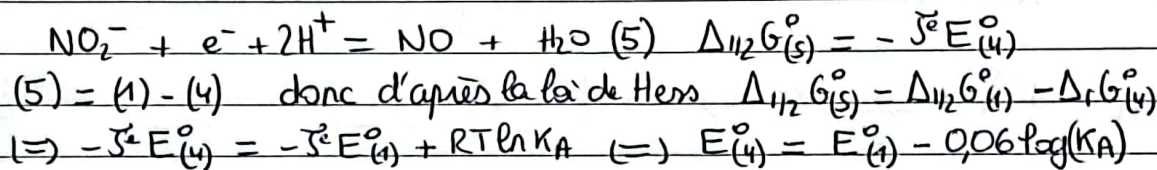
## ex 1 dismutation de l'acide nitreux



Donc  $\boxed{\log(K^\circ) = \frac{2}{0,06} (E_1^\circ - E_2^\circ)}$     AN:  $\log(K^\circ) = 1,33$

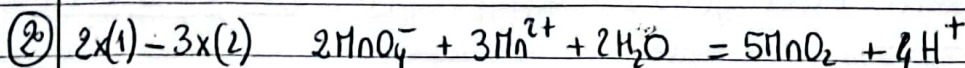
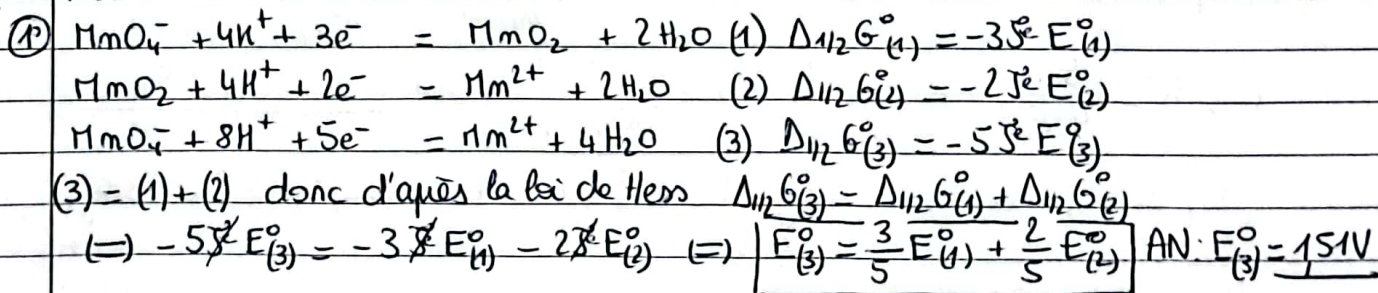


$\boxed{E_3^\circ = E_2^\circ - 0,03 \text{p}K_A}$     AN:  $E_3^\circ = 0,84 \text{V}$



$\boxed{E_4^\circ = E_1^\circ + 0,06 \text{p}K_A}$     AN:  $E_4^\circ = 1,17 \text{V}$

## ex 2 médiamutation en milieu acide



$(3^\circ) \Delta_r G^\circ = -RT \ln(K^\circ) = 2\Delta_{1/2} G^\circ_{(1)} - 3\Delta_{1/2} G^\circ_{(2)} \quad (\Rightarrow) -RT \ln(K^\circ) = 6\mathcal{J}^\circ (E_2^\circ - E_1^\circ)$   
 $\Rightarrow \boxed{\log(K^\circ) = \frac{6}{0,06} (E_1^\circ - E_2^\circ)}$     AN:  $\log(K^\circ) = 47$

$(4^\circ) [\text{Mn}^{2+}]_i = [\text{MnO}_4^-]_i = 0,05 \text{ mol.L}^{-1}$   
 $m(\text{Mn}^{2+})_i = m(\text{MnO}_4^-)_i = 10^{-3} \text{ mol} = m_0$   
 $\text{pH} = 0 \quad (\Rightarrow) [\text{H}^+] = 1 \text{ mol.L}^{-1} \quad \text{supposé constant.}$

$K^\circ = 10^{47} \rightarrow$  transfo quasi-totale.  
 $\text{Mn}^{2+}$  réactif limitant.  $\xi \approx \frac{m_0}{3}$   
 $m(\text{Mn}^{2+})_f = \xi \quad m(\text{MnO}_4^-)_f = \frac{m_0}{3} = 333 \cdot 10^{-4} \text{ mol}$   
 $m(\text{MnO}_2)_f = \frac{5}{3} m_0 = 1,67 \cdot 10^{-3} \text{ mol}$   
 $m(\text{HNO}_2)_f = 0,145 \text{ g}$

ex 3 potentiométrie

(1°)  $\text{Sn}^{4+} + 2e^- = \text{Sn}^{2+}$  d'après la formule de Nernst

$$E_{\text{Pt}} = E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + \frac{0,06}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]} = E_1^{\circ}$$

$$\boxed{U = E_{\text{Pt}} - E_{\text{ECS}}} \quad \text{AN: } \underline{U = -1,05V}$$

(2°)  $\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$  (2)  $\Delta_{1/2} G_{(2)}^{\circ} = -J^{\circ} E_2^{\circ}$

$\text{Sn}^{2+} = \text{Sn}^{4+} + 2e^-$  (1)  $\Delta_{1/2} G_{(1)}^{\circ} = 2J^{\circ} E_1^{\circ}$

$2\text{Fe}^{3+} + \text{Sn}^{2+} = 2\text{Fe}^{2+} + \text{Sn}^{4+}$  (3) = 2(2) + (1) donc d'après la loi de Hess

$$\Delta_r G_{(3)}^{\circ} = 2 \Delta_{1/2} G_{(2)}^{\circ} + \Delta_{1/2} G_{(1)}^{\circ} = 2J^{\circ} (E_1^{\circ} - E_2^{\circ}) = -RT \ln K^{\circ}$$

donc  $\log K^{\circ} = \frac{2}{0,06} (E_2^{\circ} - E_1^{\circ})$  AN:  $\log(K^{\circ}) = 21 \rightarrow$  transfo quasi-totale

$m(\text{Fe}^{3+})_i = 10^{-3} \text{ mol} = m_0$

$\text{Fe}^{3+}$  réactif limitant  $\xi_f = \frac{m_0}{2}$

$m(\text{Sn}^{2+})_i = m(\text{Sn}^{4+})_i = m_0$

$m(\text{Sn}^{2+})_f = \frac{m_0}{2}$   $m(\text{Sn}^{4+})_f = \frac{3m_0}{2}$

$$E_{\text{Pt}} = E_1^{\circ} + \frac{0,06}{2} \log(3)$$

$$\boxed{U = E_1^{\circ} - E_{\text{ECS}} + 0,03 \log(3)} \quad \text{AN: } \underline{U = -1,04V}$$

(3°)  $m(\text{Fe}^{3+})_i = 2m_0$  } mélange stoechiométrique  $\xi_f = m_0$   
 $m(\text{Sn}^{2+})_i = m_0$

$m(\text{Fe}^{3+})_f = 2\varepsilon$   $m(\text{Sn}^{2+})_f = \varepsilon$   $m(\text{Fe}^{2+})_f = 2m_0$   $m(\text{Sn}^{4+})_f = 2m_0$

D'après la loi d'action de masse:  $K^{\circ} = \frac{m(\text{Fe}^{2+})_f^2 m(\text{Sn}^{4+})_f}{m(\text{Fe}^{3+})_f^2 m(\text{Sn}^{2+})_f}$

$$\Rightarrow K^{\circ} = \frac{8m_0^3}{4\varepsilon^3} \quad (\Rightarrow) \quad \boxed{\varepsilon = m_0 \left(\frac{2}{K^{\circ}}\right)^{1/3}} \quad \text{AN: } \underline{\varepsilon = 1,26 \cdot 10^{-10} \text{ mol}}$$

$$E_{\text{Pt}} = E_1^{\circ} + 0,03 \log\left(\frac{2m_0}{\varepsilon}\right) = E_1^{\circ} + 0,03 \log\left[2\left(\frac{K^{\circ}}{2}\right)^{1/3}\right] = E_1^{\circ} + 0,03 \log(2^{2/3}) + 0,01 \log(K^{\circ})$$

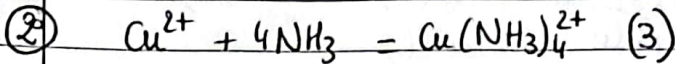
$$\boxed{E_{\text{Pt}} = E_1^{\circ} + 0,02 \log(2) + 0,01 \log(K^{\circ})} \quad U = E_{\text{Pt}} - E_{\text{ECS}} \quad \text{AN: } \underline{U = 0,11V}$$

ex4

complexation du cuivre avec l'ammoniac

①°  $Cu^{2+} + 2e^- = Cu (1)$  d'après la formule de Nernst  $E_{Cu} = E_1^{\circ} + \frac{0,06}{2} \log \left( \frac{[Cu^{2+}]}{[C^{\circ}]}\right)$

AN:  $E_{Cu} = 0,30V$



$n(Cu^{2+})_i = 2,5 \cdot 10^{-3} \text{ mol}$

$n(NH_3)_i = 5,0 \cdot 10^{-2} \text{ mol}$

$n(NH_3)_i > 4n(Cu^{2+})_i \Rightarrow NH_3 \text{ en excès}$

③° du fait de la formation du complexe,  $[Cu^{2+}]$  diminue donc le potentiel diminue de 0,360V:  $E'_{Cu} = -0,06V$

$$\beta_4 = \frac{[Cu(NH_3)_4^{2+}][C^{\circ}]^4}{[Cu^{2+}][NH_3]^4} \Leftrightarrow [Cu^{2+}] = \frac{[Cu(NH_3)_4^{2+}][C^{\circ}]^4}{\beta_4 [NH_3]^4}$$

on suppose que la réaction de complexation est quasi-totale

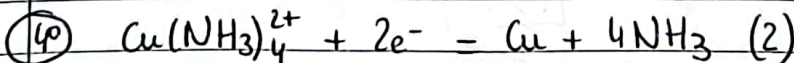
$n(Cu^{2+})_f = \xi_f = n(Cu^{2+})_i = 2,5 \cdot 10^{-3} \text{ mol}$

$[NH_3]_f = \frac{n(NH_3)_i - 4\xi_f}{V} = 0,80 \text{ mol.l}^{-1}$

$[Cu(NH_3)_4^{2+}]_f = \frac{\xi_f}{V} = 5,0 \cdot 10^{-2} \text{ mol.l}^{-1}$

$E'_{Cu} = E_1^{\circ} + 0,03 \log \left( \frac{[Cu(NH_3)_4^{2+}]_f [C^{\circ}]^3}{\beta_4 [NH_3]_f^4} \right) \Leftrightarrow \log \beta_4 = \frac{E_1^{\circ} - E'_{Cu}}{0,03} + \log \left( \frac{[Cu(NH_3)_4^{2+}]_f [C^{\circ}]^3}{[NH_3]_f^4} \right)$

AN:  $\log \beta_4 = 12,4$



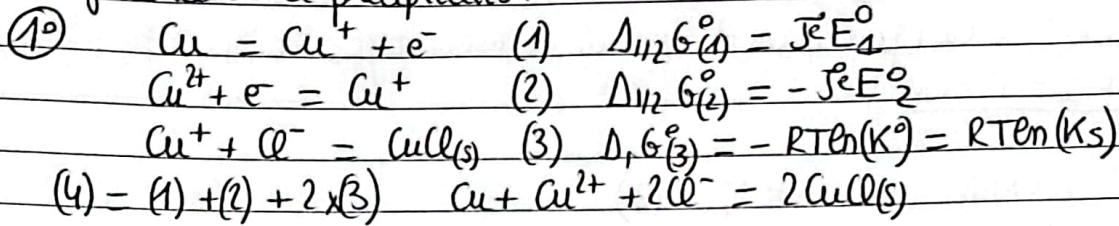
(2) = (1) - (3) donc d'après la loi de Hess  $\Delta_{1/2} G^{\circ}(2) = \Delta_{1/2} G^{\circ}(1) - \Delta_{1/2} G^{\circ}(3)$

$-2F E_2^{\circ} = -2F E_1^{\circ} + RT \ln(\beta_4) \Leftrightarrow E_2^{\circ} = E_1^{\circ} - \frac{0,06}{2} \log(\beta_4)$

$E_{Cu(NH_3)_4^{2+}/Cu}^{\circ}$

AN:  $E_2^{\circ} = 0,032V$

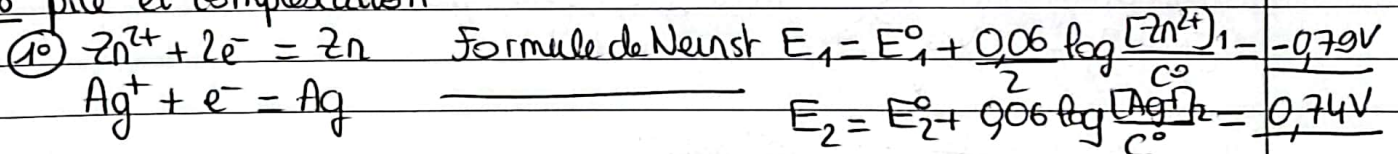
ex 5 influence de la précipitation



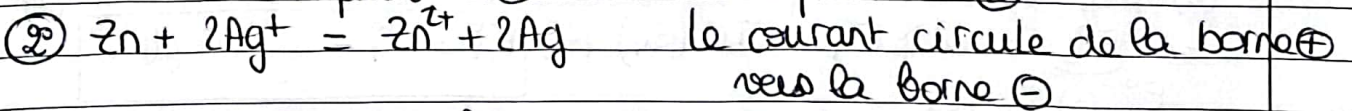
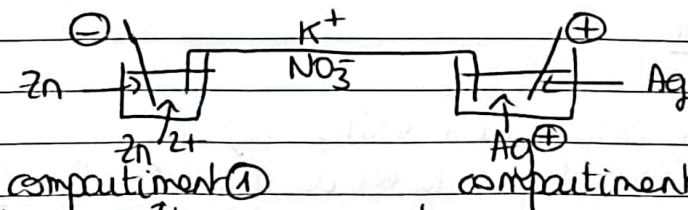
(2°) d'après la loi de Hess:  $\Delta_r G^\circ(4) = \Delta_{1/2} G^\circ(1) + \Delta_{1/2} G^\circ(2) + 2\Delta_r G^\circ(3)$   
 $\Rightarrow \Delta_r G^\circ(4) = J^\circ (E_1^\circ - E_2^\circ) + 2RT \ln(K_s)$   
 $\Rightarrow -RT \ln(K_4^\circ) = J^\circ (E_1^\circ - E_2^\circ) + 2RT \ln(K_s)$   
 $\Rightarrow \log(K_4^\circ) = \frac{E_2^\circ - E_1^\circ - 2 \log(K_s)}{0,06}$  AN:  $\log(K_4^\circ) = 13,8$

transfo quasi-totale  $\text{Cu}^{2+}$  et  $\text{Cl}^-$  en mélange stœchiométrique  
 p̄au 1L  $\xi_f = 0,10 \text{ mol} \rightarrow n(\text{CuCl})_f = 2 \xi_f = 0,20 \text{ mol}$ .

ex 8 pile et complexation

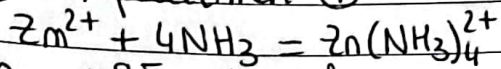


$E_1 < E_2$  borne  $\ominus$ : Zn      borne  $\oplus$ : Ag  
 $e = E_2 - E_1$   $\text{Zn} = \text{Zn}^{2+} + 2e^-$        $\text{Ag}^+ + e^- = \text{Ag}$   
 AN:  $e = 1,53 \text{ V}$       anode      cathode



(3°) ajout de  $\text{NH}_3$  dans le compartiment (1): le complexe  $\text{Zn}(\text{NH}_3)_4^{2+}$  se forme donc  $[\text{Zn}^{2+}]$  diminue donc  $E_1$  diminue et  $e$  augmente.  
 ajout de  $\text{NH}_3$  dans le compartiment (2): le complexe  $\text{Ag}(\text{NH}_3)_2^+$  se forme donc  $[\text{Ag}^+]$  diminue donc  $E_2$  diminue et  $e$  diminue.

4° compartiment ①



$\beta_4 = 10^{9,5} \rightarrow$  transfo quasi-totale

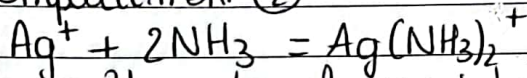
$$[\text{Zn}^{2+}]_1 = \epsilon$$

$$[\text{Zn}(\text{NH}_3)_4^{2+}]_1 = 0,1 \text{ mol.l}^{-1}$$

$$[\text{NH}_3]_1 = 1,1 \text{ mol.l}^{-1}$$

$$\beta_4 = \frac{[\text{Zn}(\text{NH}_3)_4^{2+}](\text{C}^\circ)^4}{[\text{Zn}^{2+}][\text{NH}_3]_1^4} \Leftrightarrow [\text{Zn}^{2+}]_1 = \frac{[\text{Zn}(\text{NH}_3)_4^{2+}](\text{C}^\circ)^4}{\beta_4 [\text{NH}_3]_1^4}$$

compartiment ②



$\beta_2 = 10^{7,1} \rightarrow$  transfo quasi-totale

$$[\text{Ag}^+]_2 = \epsilon$$

$$[\text{Ag}(\text{NH}_3)_2^+]_2 = 0,1 \text{ mol.l}^{-1}$$

$$[\text{NH}_3]_2 = 0,8 \text{ mol.l}^{-1}$$

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]_2 (\text{C}^\circ)^2}{[\text{Ag}^+]_2 [\text{NH}_3]_2^2} \Leftrightarrow [\text{Ag}^+]_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]_2 (\text{C}^\circ)^2}{\beta_2 [\text{NH}_3]_2^2}$$

$$e = E_2^\circ - E_1^\circ + 0,06 \log \left( \frac{[\text{Ag}(\text{NH}_3)_2^+]_2 (\text{C}^\circ)^2}{\beta_2 [\text{NH}_3]_2^2} \right) - 0,03 \log \left( \frac{[\text{Zn}(\text{NH}_3)_4^{2+}]_1 (\text{C}^\circ)^4}{\beta_4 [\text{NH}_3]_1^4} \right)$$

AN:  $e = 1,41 \text{ V}$