Exo : pile fer / Etain.

1- $Fe^{3+} + e^- = Fe^{2+}$ (1)

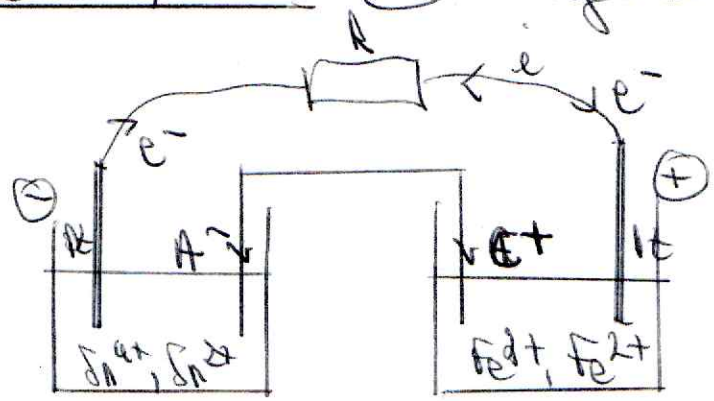
$E_1 = E_1^0 + 0,06 \log\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right)$

$E_1 = 0,79\,V$ ⊕ réduction, cathode

$Sn^{4+} + 2e^- = Sn^{2+}$ (2)

$E_2 = E_2^0 + 0,03 \log\left(\frac{[Sn^{4+}]}{[Sn^{2+}]}\right)$

$E_2 = 0,12\,V$ ⊖ oxydation, anode.



2- $e = E_1 - E_2 = 0,67\,V$

4- $2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$ (3)

1ère méthode :

$E_1 = E_2$ à l'eq.

$E_1^0 + \frac{0,06}{2} \log\left(\frac{[Fe^{3+}]^2}{[Fe^{2+}]^2}\right) = E_2^0 + 0,03 \log\left(\frac{[Sn^{4+}]}{[Sn^{2+}]}\right)$

$0,03 \log(K^0) = E_1^0 - E_2^0$

$K^0 = 10^{\frac{E_1^0 - E_2^0}{0,03}} = 10^{21,3}$ ⇒ réaction totale

2ème méthode :

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

$\Delta_r G_3^\circ = 2 \Delta_r G_1^\circ - \Delta_r G_2^\circ$

$-RT \ln K^\circ = -2FE_1^\circ + 2FE_2^\circ$

$\frac{RT}{F} \ln K^\circ = 2(E_1^\circ - E_2^\circ)$

à 25°C $\quad 0,06 \log(K^\circ) = 2(E_1^\circ - E_2^\circ)$

$K^\circ = 10^{\frac{(E_1^\circ - E_2^\circ)}{0,03}} = 10^{44,3}$

Ex 5: Mesure enthalpie standard de dissolution.

(4) $HCl_{(g)} = H^+_{(aq)} + Cl^-_{(aq)}$

$\ominus$ Pt / $H_{2(g)}$, 1 bar / $H^+_{(aq)}$ + $Cl^-_{(aq)}$ // $AgCl_{(s)}$ / $Ag_{(s)}$ $\oplus$

1 - Pôle $\oplus$: réduction.

(1) $AgCl_{(s)} + e^- = Ag_{(s)} + Cl^-_{(aq)}$ $\oplus$

Pôle $\ominus$: oxydation.

(2) $H_{2(g)} = 2H^+_{(aq)} + 2e^-$ $\ominus$

Eq bilan (1) $- \frac{(2)}{2}$

3) $AgCl_{(s)} + \frac{1}{2}H_{2(g)} = Ag_{(s)} + H^+_{(aq)} + Cl^-_{(aq)}$

Fem. $E^\circ = -\frac{\Delta_r G^\circ}{F} = -\frac{\Delta_r G_1^\circ - \frac{\Delta_r G_2^\circ}{2}}{F}$

$$E^\circ = -\frac{\nu^\circ(Ag) + \nu^\circ_{H^+} + \nu^\circ_{Cl^-} - \nu^\circ_{AgCl} - \frac{1}{2}\nu^\circ_{H_2}}{F}$$

2 - $E^\circ = 0,222\ V$ $\quad \frac{dE^\circ}{dT} = -6,00 \cdot 10^{-4}\ V \cdot K^{-1}$

$E^\circ = -\frac{\Delta_r G^\circ}{F}$ $\quad \frac{dE^\circ}{dT} = \frac{1}{F} \times \frac{d(-\Delta_r G^\circ)}{dT} = \frac{\Delta_r S^\circ}{F}$

$\Delta_r G^\circ = +\Delta_r H^\circ - T\Delta_r S^\circ \Rightarrow \Delta_r S^\circ = \frac{\Delta_r H^\circ}{T} - \frac{\Delta_r G^\circ}{T}$

$-\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ$

$\Delta_r H^\circ = -FE^\circ + TF\frac{dE^\circ}{dT}$

$\Delta_r H^\circ = -38,7\ kJ \cdot mol^{-1}$

3 - (3) s'écrit comme combinaison linéaire des réactions suivantes :

(a) $Ag_{(s)} + \frac{1}{2} Cl_{2(g)} = AgCl_{(s)}$

(b) $\frac{1}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} = HCl_{(g)}$

(c) $HCl_{(g)} = Cl^-_{(aq)} + H^+_{(aq)}$

(3) = -(a) + (b) + (c)

$\Delta_r H^\circ_3 = -\Delta_f H^\circ(AgCl) + \Delta_f H^\circ(HCl) + \Delta_{diss} H^\circ(HCl)$

$\Delta_{diss} H^\circ(HCl) = \Delta_r H^\circ_3 + \Delta_f H^\circ(AgCl) - \Delta_f H^\circ(HCl)$

$\underline{\Delta_{diss} H^\circ(HCl) = -73,5 \text{ kJ.mol}^{-1}}$

Ex 6 : Dismutation de l'acide nitreux.

1 - $\overset{+III}{HNO_2} + H^+ + e^- = \overset{+II}{NO_{(g)}} + H_2O$ (1).

$\overset{V}{NO_3^-}$, $\overset{+III}{HNO_2}$

$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$ (2)

Dismutation de HNO_2 : 2x(1) - (2).

$3\,HNO_2 = 2NO + NO_3^- + \underbrace{H^+ + H_2O}_{H_3O^+}$.

2 - Données :

$HNO_2 = NO_2^- + H^+$ K_A. (a)

$NO_2^- + 2H^+ + e^- = NO + H_2O$ (b)

$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$ (c)

(1) = (b) + (a)

$\Delta_r G_1^\circ = \Delta_r G_b^\circ + \Delta_r G_a^\circ$

$-FE_1^\circ = -FE_b^\circ - RT \ln K_A$.

$E_1^\circ = E_b^\circ + 0{,}06 \log K_A = E_b^\circ - 0{,}06\, pK_a$.

$\underline{E_1^\circ(HNO_2/NO) = 0{,}98\ V}$.

(2) = (c) − (a)

$\Delta_r G_2^\circ = \Delta_r G_c^\circ - \Delta_r G_a^\circ$

$-2FE_2^\circ = -2FE_c^\circ + RT \ln K_a$

$E_2^\circ = E_c^\circ - \frac{0,06}{2} \log K_a$

$E_2^\circ = E_c^\circ + 0,03\, pK_a$

$\underline{E_2^\circ = 0,95\,V = E^\circ(NO_3^-/HNO_2)}$

3 − $\Delta_r G^\circ = 2\Delta_r G_a^\circ - \Delta_r G_2^\circ$

$= -2FE_1^\circ + 2FE_2^\circ$

$\underline{\Delta_r G^\circ = -5790\ J.mol^{-1}}$

4 − $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ Statt de.

$\Delta_r G = \Delta_r G^\circ + RT \ln \left(\frac{P_{NO}^2 [NO_3^-][H_3O^+]}{[HNO_2]^3} \right) < 0$

$\frac{P_{NO}^2 [NO_3^-][H_3O^+]}{P^{\circ 2} [HNO_2]^3} < K^\circ = e^{-\frac{\Delta_r G^\circ}{RT}} = 10,4$

$P_{NO} < \left(\frac{10,4 [HNO_2]^3}{[NO_3^-][H_3O^+]} \right)^{1/2} \times P^\circ$

$[HNO_2] = 10^{-2} mol.l^{-1}$

$[NO_3^-] = 10^{-2} mol.l^{-1}$

$= [H_3O^+]$

$\underline{P_{NO} < 10,2\ bar}$