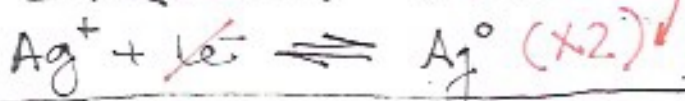
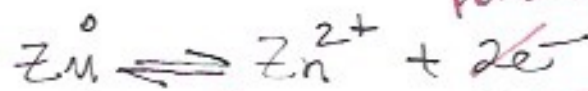
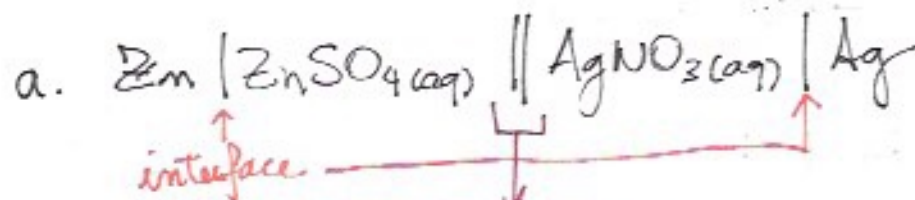


QFL 2427

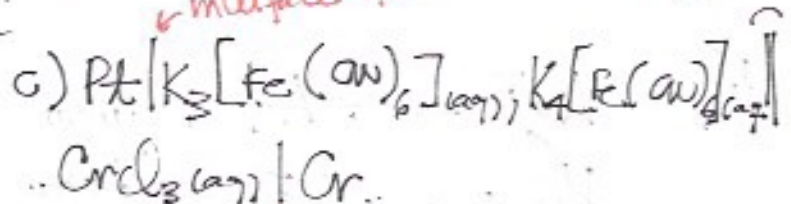
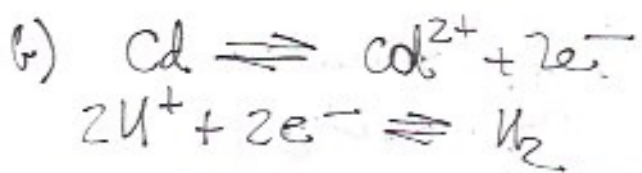
LISTA DE PROBLEMAS "TERMODINÂMICA & ELETROQUÍMICA"

1. Convenções: **Esquerda Oxidação**
Direita Redução

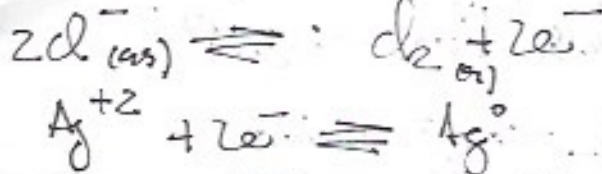
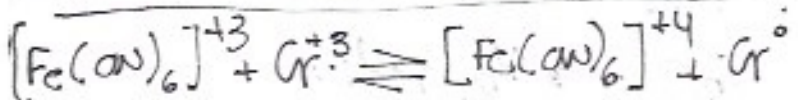
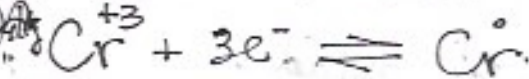
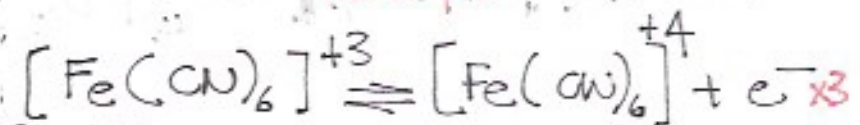


REAÇÃO DA PILHA

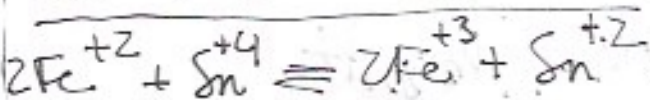
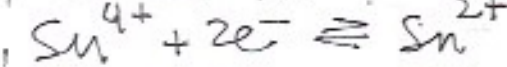
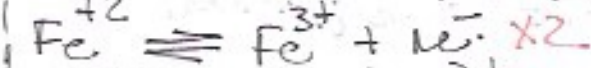
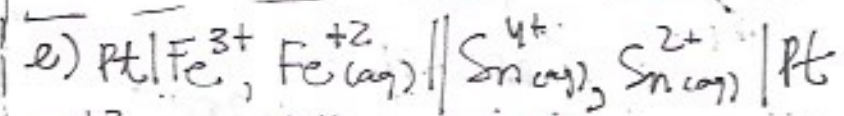
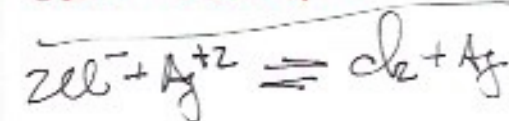
interface fio de Pt. com solução
ponte salina

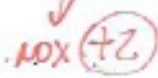
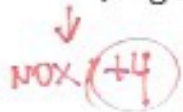
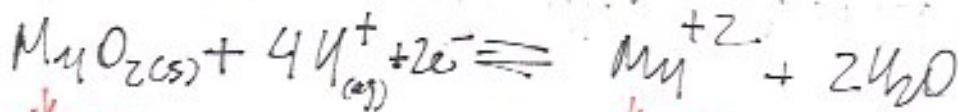
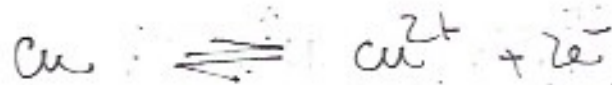
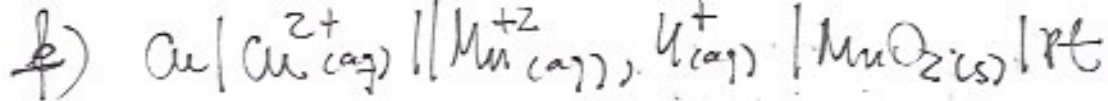


interface Cr metálico solução

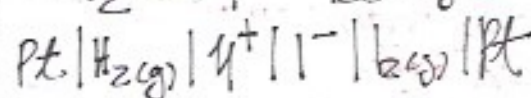
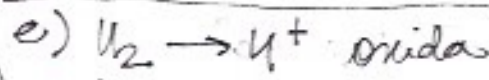
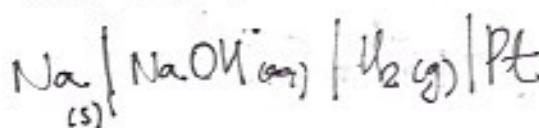
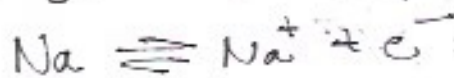
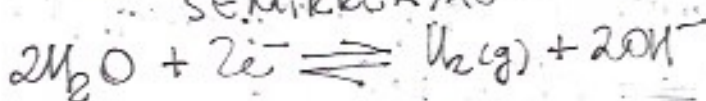
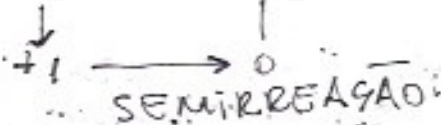
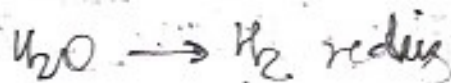
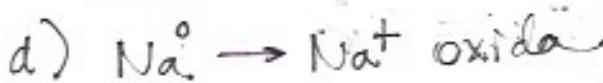
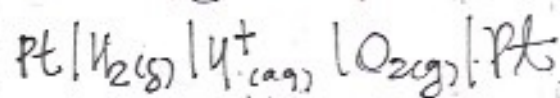
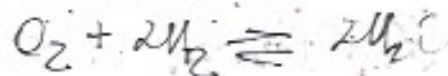
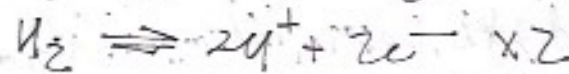
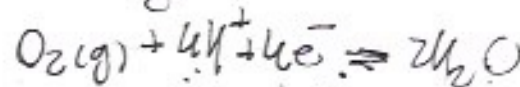
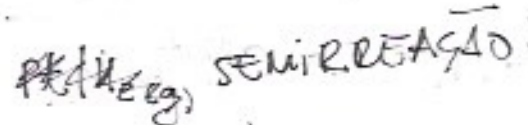
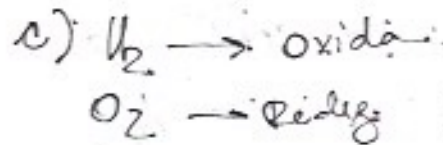
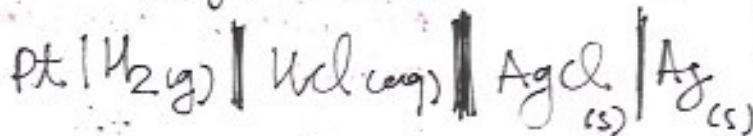
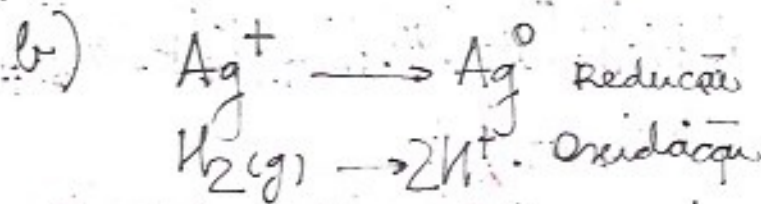
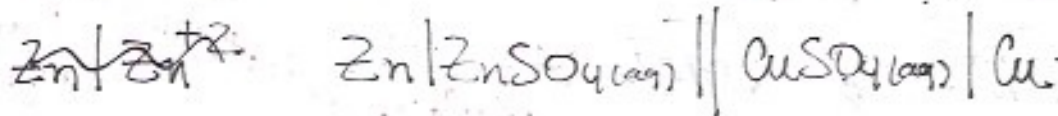
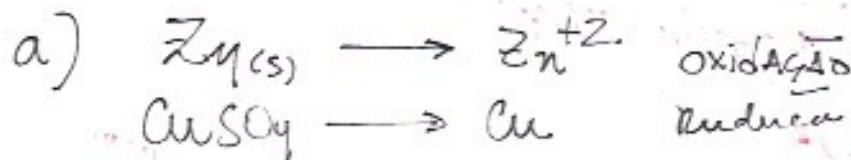


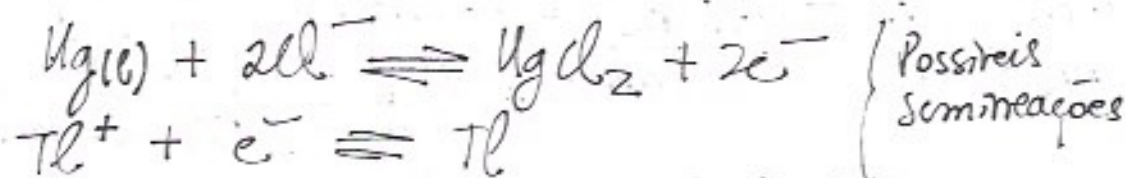
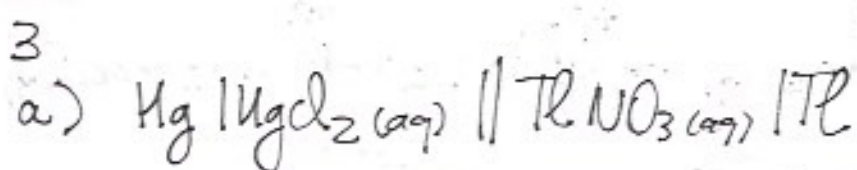
** O CrO_4^{2-} não muda de estado de Oxidação*



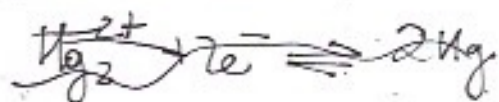


2. Na mesma lógica do f):

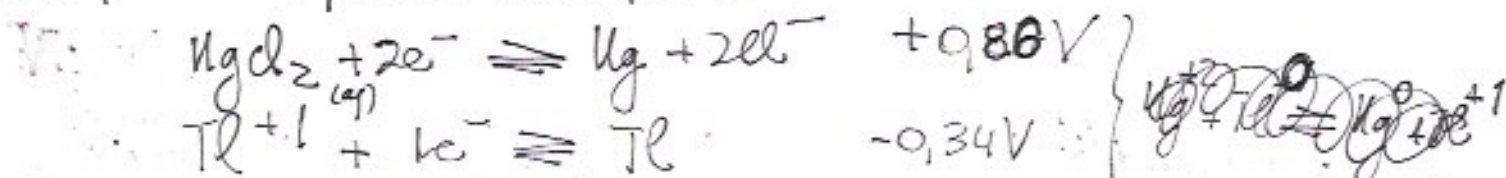




Os potenciais padrão são:



Os potenciais padrão de redução são:



Como $\Delta E^\circ = E^\circ_{\text{direita}} - E^\circ_{\text{esquerda}}$
 redução *oxidação*

$$= -0,34 - (0,86) = -1,20\text{V}$$

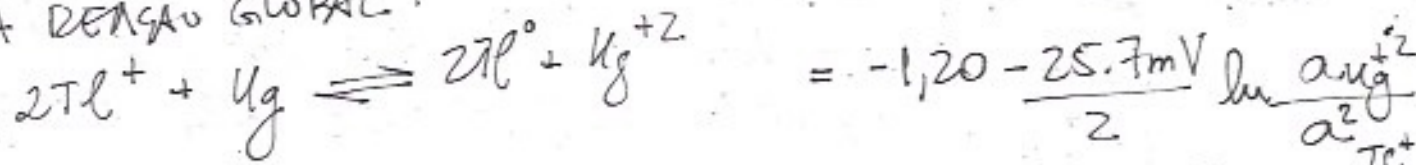
$$E^\circ = -1,20\text{V} \text{ como } \Delta G^\circ = -nFE^\circ = -1,20 \times 2 \cdot F$$

A reação acontece no sentido oposto

Temos que

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{25,7\text{mV}}{2} \ln \frac{a_{\text{Tl}}^2 \cdot a_{\text{Hg}}^{+2}}{a_{\text{Tl}^+}^2 \cdot a_{\text{Cl}^-}^2}$$

A REAÇÃO GLOBAL:

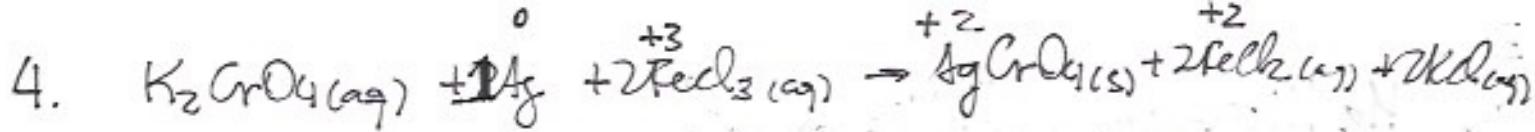


$$= -1,20 - \frac{25,7\text{mV}}{2} \ln \frac{0,15}{0,95^2}$$

$$= -1,20 - \frac{25,7\text{mV}}{2} \times -1,77$$

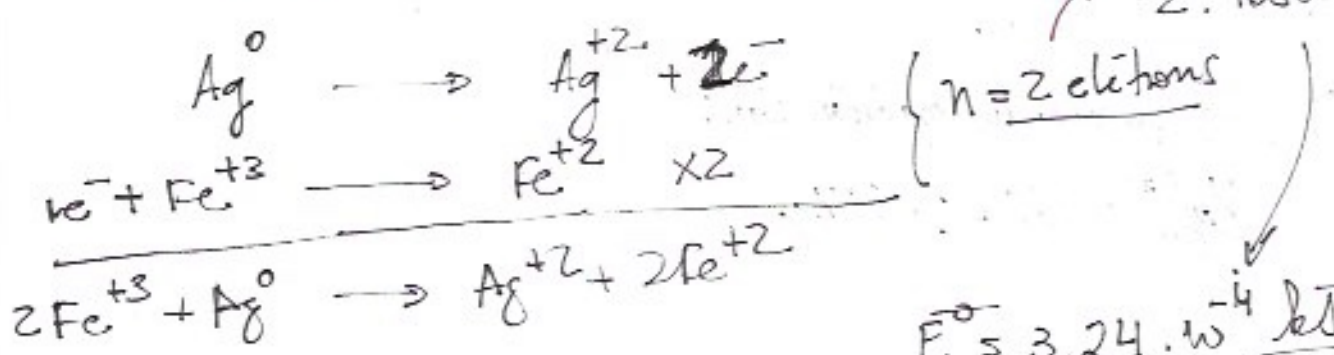
$$= -1,20 + 0,023$$

$$= -1,177\text{V}$$



$$\Delta G^\circ = -nFE^\circ \therefore -62,5 \frac{\text{kJ}}{\text{mol}} = -n \cdot F \cdot E^\circ$$

SEMIRREAÇÕES: $\Rightarrow E^\circ = \frac{-62,5 \text{ kJ} \cdot \text{mol}^{-1}}{2 \cdot 96500 \text{ C} \cdot \text{mol}^{-1}}$

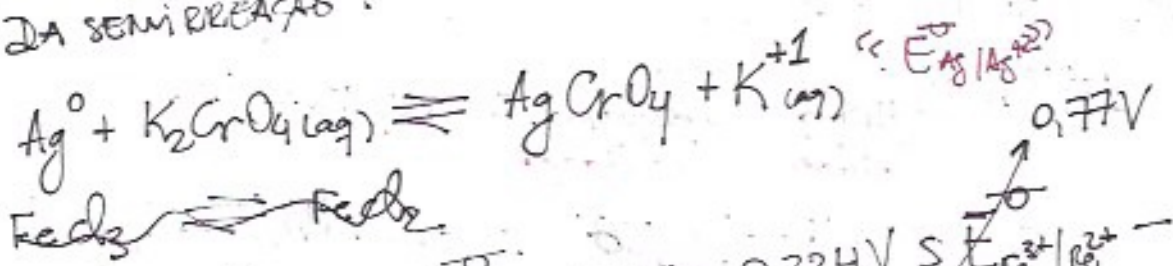


$$E^\circ = 3,24 \cdot 10^{-4} \frac{\text{kJ}}{\text{C}} = 0,324 \frac{\text{J}}{\text{C}}$$

$$W = q \cdot V$$

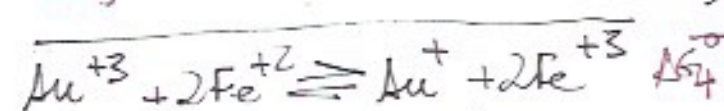
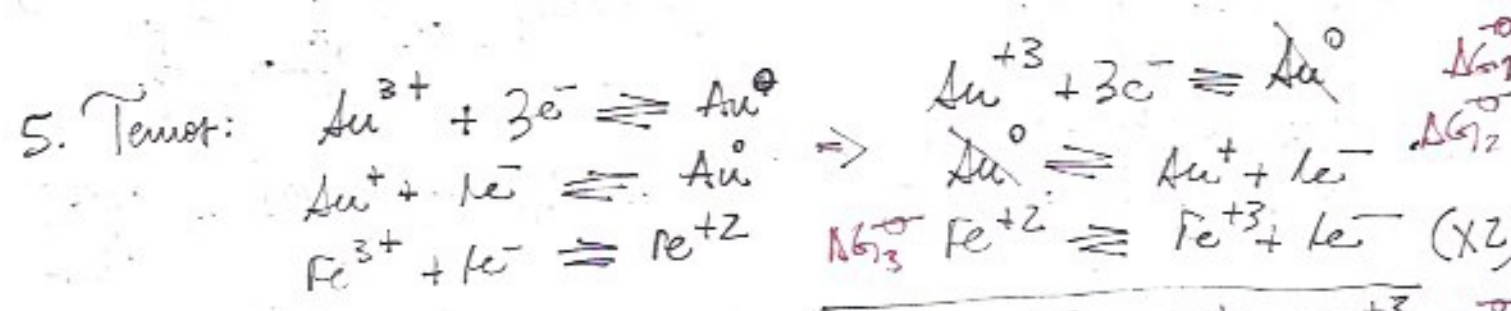
Trabalho elétrico

b) DA SEMIRREAÇÃO:



$$E^\circ_{\text{célula}} = E^\circ_{\text{redução}} - E^\circ_{\text{oxidação}} \Rightarrow 0,324 \text{V} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^\circ_{\text{Ag}^0/\text{Ag}^{+2}}$$

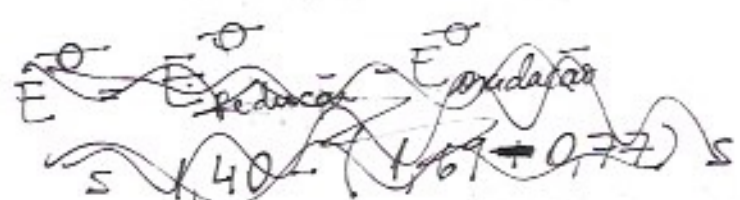
$$\therefore E^\circ_{\text{Ag}^0/\text{Ag}^{+2}} = -(0,324 - 0,77) = 0,446 \text{V}$$



Do ciclo termodinâmico.

$$\Delta G_4^\circ = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$$

$$= -nFE^\circ_{\text{Au}^{3+}/\text{Au}^0} + n_2FE^\circ_{\text{Au}^0/\text{Au}^+} + n_3FE^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$$



$$\therefore \Delta G_4^\circ = -3F \cdot 1,40 + 1 \cdot F \cdot 1,69 + 1 \cdot F \cdot 0,77$$

$$\Rightarrow \Delta G_4^\circ = -1,74F = -n \cdot E^\circ \cdot F$$

$$\Rightarrow -1,74 \times 96500 = -2 \cdot E^\circ \cdot 96500 \therefore E^\circ = 0,87 \text{V}$$

Os sinais estão trocados pois as reações estão invertidas (4)

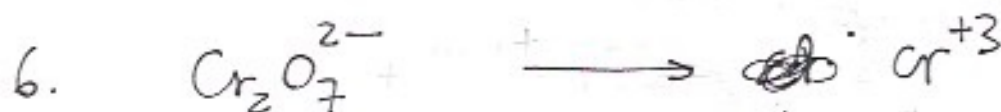
Logo A CONSTANTE DE EQUILIBRIO E:

$$\Delta G^{\circ} = -RT \ln K^{\circ} \dots -E^{\circ} n F = -nRT \ln K^{\circ} \Rightarrow K^{\circ} = \exp \left[\frac{E^{\circ} n F}{RT} \right]$$

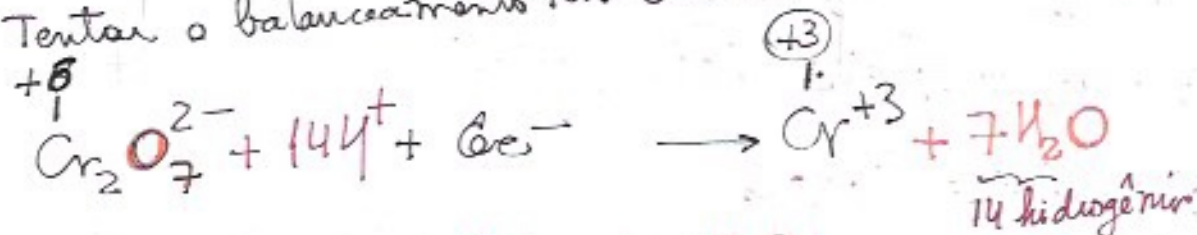
$$K^{\circ} = \exp \left[\frac{+1,74 F}{RT} \right] = \exp \left[\frac{1,74 \times 96500 \text{ C} \cdot \text{mol}^{-1} \cdot \text{V}}{8,31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}} \right]$$

C.V = J

$$\Rightarrow e^{67,8} = K^{\circ}$$



Tentar o balanceamento ion-elétron:



i) Balancear o oxigênio com H_2O

ii) Acrescentar os hidrogênios com H^+

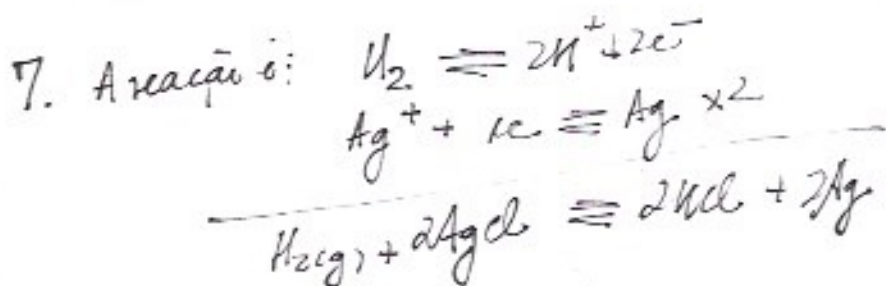
iii) Acrescentar os e^- , no caso os fomo 3e^- por átomo de Crômio

Esta seria a célula, logo, as semirreações são: uma célula contra o eletrodo padrão de hidrogênio. O E° tabelado é $+1,33 \text{ V}$ (para tal reação)

A equação do potencial fica

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{H}_2} \cdot a_{\text{Ag}}^2}{a_{\text{H}^+}^2 \cdot a_{\text{AgCl}}^2}$$

como AgCl e $\text{H}_2(\text{g})$ são fases condensadas $a_{\text{AgCl}} = a_{\text{H}_2} = 1$



$$E = E^{\circ} - \frac{RT}{nF} \ln a_{\text{HCl}}^2 = E^{\circ} - \frac{2RT}{nF} \ln a_{\text{HCl}} \dots$$

$$0,322 \text{ V} = 0,222 \text{ V} - \frac{2}{2} \cdot \frac{8,31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}}{96500 \text{ C} \cdot \text{mol}^{-1}} \cdot \ln a_{\text{HCl}}$$

$$= J = C \cdot V$$

$$J/C = \text{Volts}$$

$$\frac{-0,1 \text{ V}}{0,025 \text{ V}} = \ln a_{\text{HCl}} \Rightarrow -4 = \ln a_{\text{HCl}} \Rightarrow a_{\text{HCl}} = e^{-4} \therefore \text{se } [\text{HCl}] \approx a_{\text{HCl}}$$

$$[\text{HCl}] = [\text{H}^+] = e^{-4} \therefore \text{pH} = -\log e^{-4} = +4 \log e = 1,73$$

8. A solubilidade é: $AgBr(s) \rightleftharpoons Ag^+ + Br^-$

$K_{ps} = a_{Ag^+} \cdot a_{Br^-}$ como a solução é diluída:

$$a_{Ag^+} \approx [Ag^+] = S \quad \therefore K_{ps} \approx S^2 = \left(\frac{2,6 \mu\text{mol}}{\text{kg}} \right)^2$$

$$a_{Br^-} \approx [Br^-] = S$$

A concentração está em molalidade de mol soluto / kg solvente

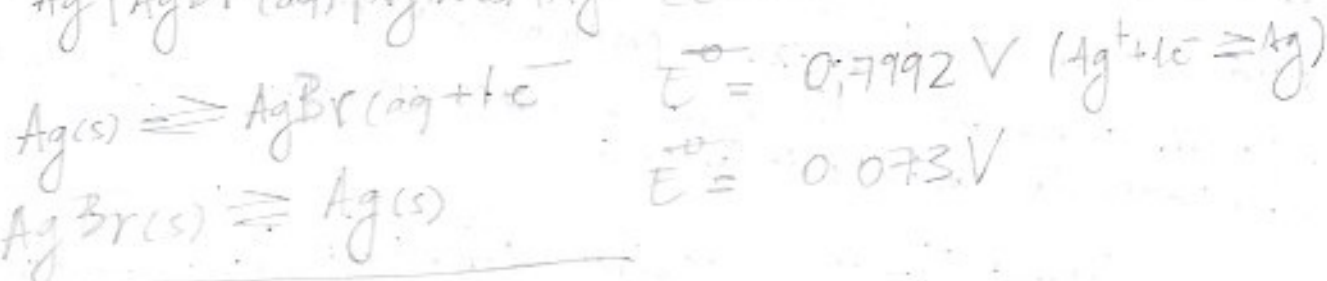
como $\Delta G^\circ = -nFE^\circ = -RT \ln K^\circ$

$$\therefore E^\circ = \frac{RT}{nF} \ln K^\circ = \frac{RT}{nF} \ln S^2$$

$$= \frac{2RT}{nF} \ln S = \frac{2 \cdot 8,31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 298 \text{ K}}{1 \cdot 96500 \text{ C} \cdot \text{mol}^{-1}} \ln 2,6 \cdot 10^{-6} \frac{\text{mol}}{\text{kg}}$$

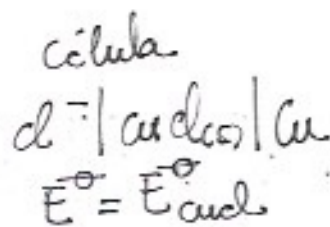
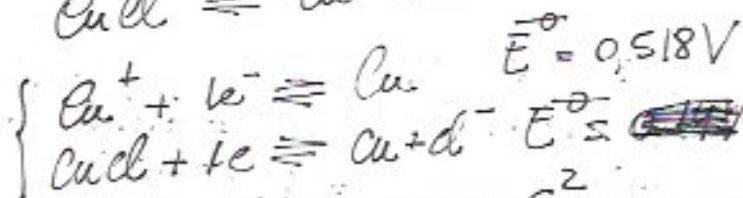
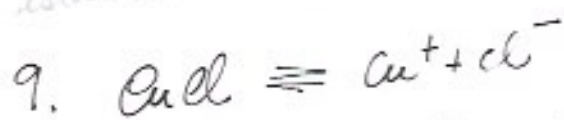
$$= 0,0513 \times -12,8 = -0,659 \text{ V}$$

II) $Ag | AgBr(aq) | AgBr(s) | Ag$ CÉLULA EM QUESTÃO



Assim, $E^\circ = E_{red}^\circ - E_{oxi}^\circ = 0,073 - 0,7992 = -0,7262$

Este quadro em lápis é apenas para mostrar que um valor muito próximo pode ser obtido com as aproximações. A diferença nos valores obtidos deve-se ao fato do constante de equilíbrio calculada estar em escala de molalidade

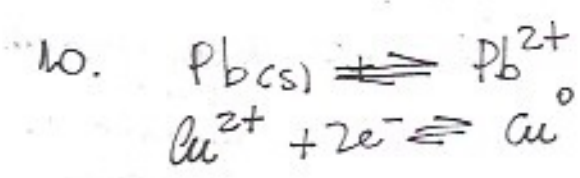


Como em 8) $E^\circ = \frac{RT}{F} \ln S^2 = \frac{2RT}{F} \ln S = 0,0513 \ln 2,29 \cdot 10^{-7}$

$$= 0,0513 \times -15,3 = -0,778 \text{ V}$$

$$E^\circ = E_{CuCl}^\circ - E_{Cu^+/Cu}^\circ \quad \therefore -0,778 = E_{CuCl}^\circ - 0,518 \Rightarrow E_{CuCl}^\circ = 0,262 \text{ V}$$

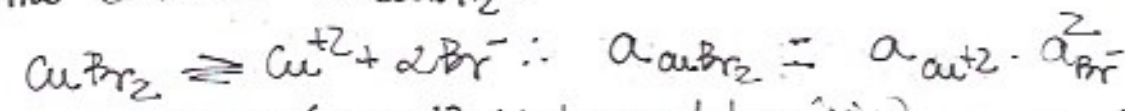
b) $Cu^+ + Cl^- \rightleftharpoons CuCl \quad \Delta G = -\Delta G_{CuCl \rightarrow Cu^+ + Cl^-}$
 $\therefore \Delta G = -(-1.96500 \cdot -0.78) = -75 \text{ kJ/mol}$



a) $Cu | CuBr(aq, 0.0100 \text{ molal}) | PbBr(s) | Cu(s)$

b) $E = E^\ominus - \frac{RT}{nF} \ln \frac{a_{PbBr} \cdot a_{Cu}}{a_{CuBr_2} \cdot a_{Pb}} = E^\ominus - \frac{RT}{nF} \ln \frac{1}{a_{CuBr_2}}$

Como calcular a_{CuBr_2} ?



VIDE LEVINE CAPÍTULO 13 (sistemas eletroquímicos)

Para o eletrólito $M_{v+}X_{v-}$ o produto de atividade é $a_+^{v+} \cdot a_-^{v-}$
 Seja m a molalidade do sal, temos que m_+ e m_- são as molalidades do cátion e do ânion:

$m_+ = v_+ m$
 $m_- = v_- m$

assim $a_+^{v+} \cdot a_-^{v-} = \gamma_+^{v+} \cdot \gamma_-^{v-} \cdot m_+^{v+} \cdot m_-^{v-}$
 $= \gamma_+^{v+} \cdot \gamma_-^{v-} \cdot v_+^{v+} \cdot m^{v+} \cdot v_-^{v-} \cdot m^{v-}$
 $= \gamma_+^{v+} \cdot \gamma_-^{v-} \cdot v_+^{v+} \cdot v_-^{v-} \cdot m^{v_++v_-}$

$\gamma_{\pm}^v \equiv \gamma_+^{v+} \cdot \gamma_-^{v-}$ é uma média geométrica.
 $v \equiv v_+ + v_- \therefore (v_{\pm})^v \equiv v_+^{v+} \cdot v_-^{v-}$
 Atividade iônica média

$a_+^{v+} \cdot a_-^{v-} = \gamma_{\pm}^v \cdot v_{\pm}^v \cdot m^v$

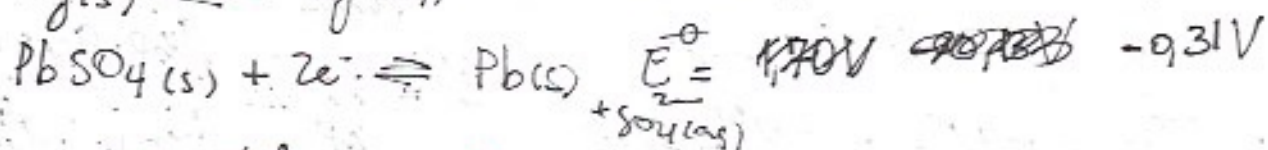
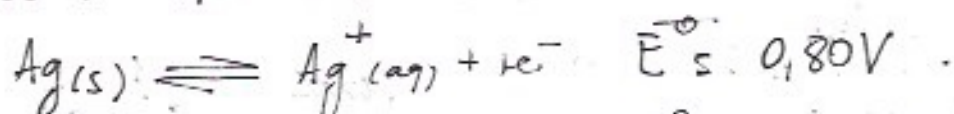
Assim: $a_{CuBr_2} = a_{Cu}^1 \cdot a_{Br}^2 = \gamma_{\pm}^3 \cdot (1) \cdot (2) \cdot 0.0100 = 4 \cdot 1 \cdot 10^{-0.45} \cdot 10^{-2}$
 $= 4 \cdot 10^{-2.45}$

Logo $E = E^\ominus - \frac{RT}{nF} \ln \frac{1}{4 \cdot 10^{-2.45}} \Rightarrow 0.442 = E^\ominus + \frac{8.31 \cdot 298}{1.96500} \ln 4 \cdot 10^{-2.45}$

0.442 = $E^\ominus + 22,56 \times 0,025 \therefore E^\ominus = 1.02V$

(7)

11. As SEMIRREAÇÕES SÃO:



A equação de Nernst fica:

~~$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Pb}} \cdot a_{\text{Ag}^+} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{Ag}} \cdot a_{\text{PbSO}_4}}$$~~

~~$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Ag}^+} \cdot a_{\text{SO}_4^{2-}}}{1}$$~~

Como $\Delta G = -nFE$, temos:

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad \times (-nF) \quad \text{Eq. de Nernst.}$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{no equilíbrio } \Delta G = 0 \text{ e } Q = K$$

$$\Delta G^\circ = -RT \ln K \rightarrow \Delta G^\circ = -nFE^\circ = -RT \ln K$$

$$K = e^{\frac{nFE^\circ}{RT}}$$

Das semirreações vem que:

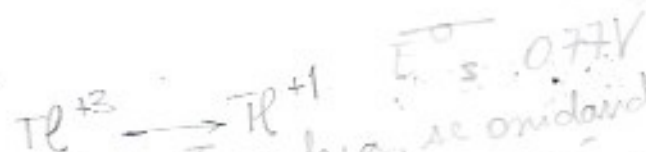
$$E^\circ = -0,31 - 0,80V = -1,11V$$

$$\therefore K = e^{\frac{-2.96500 \cdot 1,11}{8,31 \cdot 278}}$$

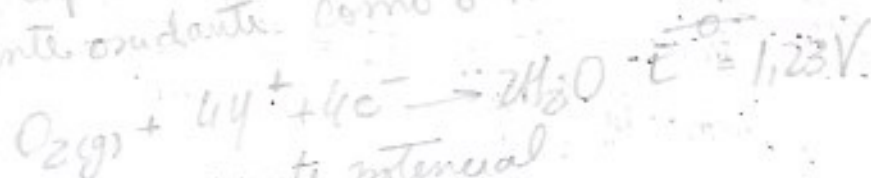
$$K = e^{-86}$$

que $\ll 1$ logo o equilíbrio está deslocado para reagentes

13. Temos



se foi exposto a atmosfera, se oxidado, o O_2 deve ter feito o papel de agente oxidante. Como o meu é o outro, temos:

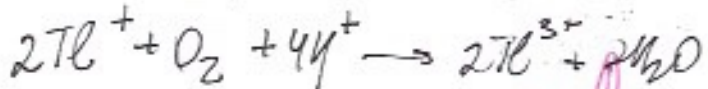
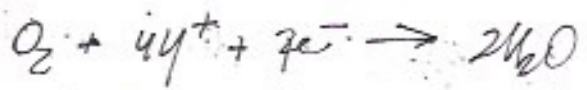
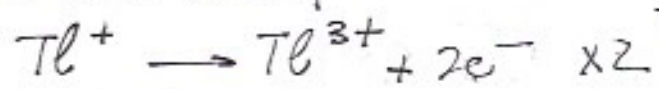


Apilha tem o seguinte potencial:

$$E^\circ = E^\circ_{\text{O}_2/\text{H}_2\text{O}} - E^\circ_{\text{Ti}^{2+}/\text{Ti}^{3+}} = 1,23 - 0,77 = 0,46V$$



SE O EQUILIBRIO FOI ALCANÇADO $\Delta G = 0$



i	x	y	z	0	0
r	-2x	-y	-4x	+2x	2y
e	x-2y	y-x	-4x	+2x	-2y

Temas

$$E^{\circ} = \frac{RT}{nF} \ln \frac{a_{H_2O} \cdot a_{Tl^{3+}}^2}{a_{Tl^+}^2 \cdot P_{O_2} \cdot a_{H^+}^4}$$

$$E^{\circ} = \frac{RT}{nF} \ln \left(\frac{a_{Tl^{3+}}}{a_{Tl^+}} \right)^2 \cdot \left(\frac{1}{a_{H^+}} \right)^4$$

SE $a \approx []$:

$$E^{\circ} = \frac{RT}{nF} \left[2 \ln \frac{[Tl^{3+}]}{[Tl^+]} - 4 \ln [H^+] \right]$$

$$0,46 = \frac{8,31 \cdot 298}{4 \cdot 96500} \times \left[2 \cdot \ln R - 4 \ln 10^{-7} \right]$$

$$72 = 2 \ln R - 0 \quad \therefore \ln R = 36 \quad \therefore R = e^{36}$$

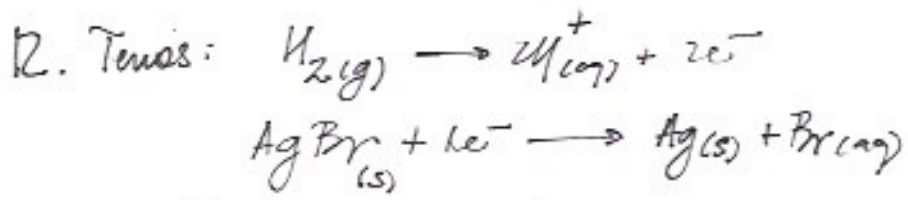
$$\frac{[Tl^{3+}]}{[Tl^+]} = e^{36} \quad \therefore \frac{n_{reagin}}{n_{inicial} - n_{reagin}} = \frac{n}{n_0 - n} = e^{36}$$

$$\therefore \frac{n}{0,1 - n} = e^{36} \quad \therefore n = (0,1 - n) e^{36} \Rightarrow n = 0,1 e^{36} - e^{36} n$$

$$n(1 + e^{36}) = 0,1 e^{36}$$

$$n = \frac{0,1 e^{36}}{1 + e^{36}} = 0,05$$

logo a quantidade de $[Tl^+]$ que reagiu é 0,05 M. $\therefore [Tl^+]_{nao\ reagiu} = 0,1 - 0,05 = 0,05 M$



A expressão fica

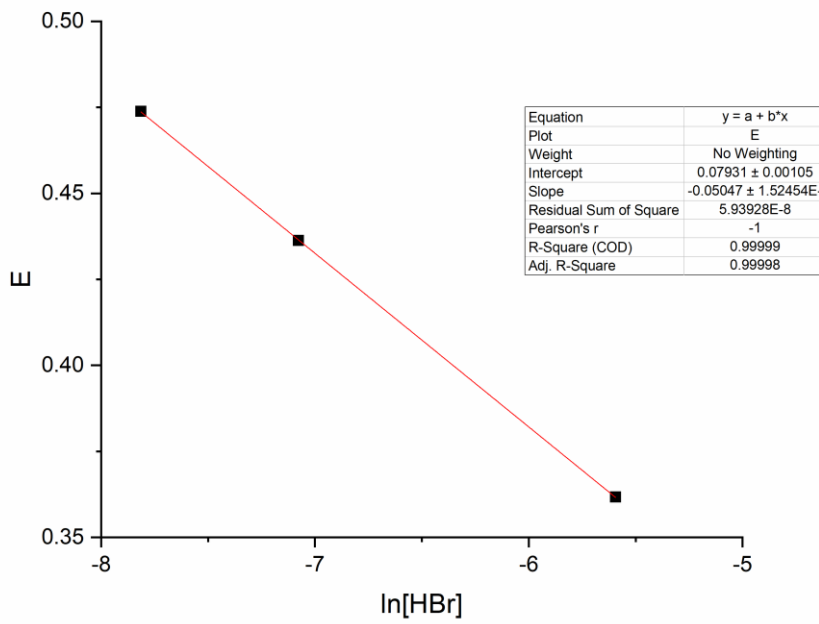
$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{Ag} \cdot a_{Br^-(aq)} \cdot a_{H^+}^2}{a_{AgBr} \cdot P_{H_2} \cdot 2 \text{atm}}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln a_{Br^-} \cdot a_{H^+}^2$$

SE $a_{Br^-} \approx [Br^-]$ e $a_{H^+} = [H^+]$ (soluções diluídas)

$$E = E^{\circ} - \frac{2RT}{nF} \ln [HBr] \quad \therefore E = E^{\circ} - \frac{RT}{F} \ln [HBr]$$

Assim, o coeficiente linear do gráfico de E contra $\ln[\text{HBr}]$ é o potencial padrão de redução



Que é 0,07931 V