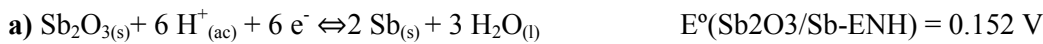


## RESOLUCIÓN DE EJERCICIOS DE PARES GALVÁNICOS EN CIRCUITO ABIERTO

### Ejercicio 1



$$E = E^\circ_{(\text{Sb}_2\text{O}_3/\text{Sb-ENH})} + RT/6F \ln[\text{H}^+]^6$$

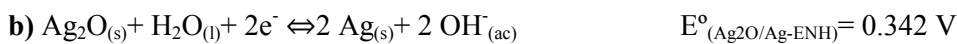
Tomando  $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ;  $T = 298 \text{ K}$ ;  $F = 96500 \text{ C mol}^{-1}$ ;  $\ln x = \ln 10 * \log x$  entonces:

$$E = E^\circ_{(\text{Sb}_2\text{O}_3/\text{Sb-ENH})} + (0.059/6) \log[\text{H}^+]^6$$

Como  $\text{pH} = -\log[\text{H}^+]$

$$E = E^\circ_{(\text{Sb}_2\text{O}_3/\text{Sb-ENH})} - 0.059 \text{ pH}$$

NOTA: En ocasiones resulta conveniente utilizar logaritmo decimal, por ejemplo para introducir pH. De cualquier forma puede operarse utilizando logaritmo neperiano para resolver la ecuación de Nernst.



$$E = E^\circ_{(\text{Ag}_2\text{O}/\text{Ag-ENH})} + (0.059/2) \log [1/[\text{OH}^-]^2]$$

$$E = E^\circ_{(\text{Ag}_2\text{O}/\text{Ag-ENH})} - 0.059 \log[\text{OH}^-]$$



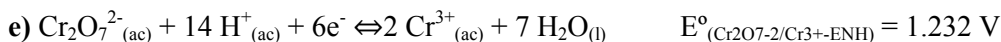
$$E = E^\circ_{(\text{Na}^+/\text{Na}(\text{Hg})\text{-ENH})} + 0.059 \log[[\text{Na}^+]/[\text{Na}(\text{Hg})]]$$



$$E = E^\circ_{(\text{Ti}^{3+}/\text{Ti}^+\text{-ENH})} + RT/2F \ln [(\text{Ti}^{3+})/(\text{Ti}^+)]$$

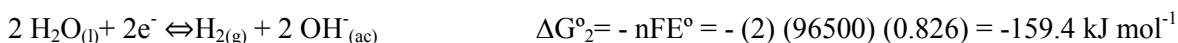
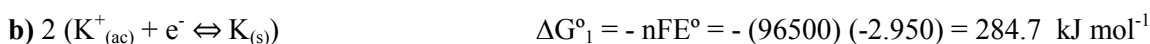
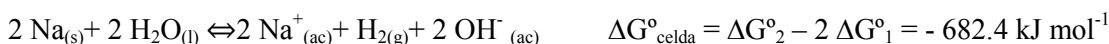
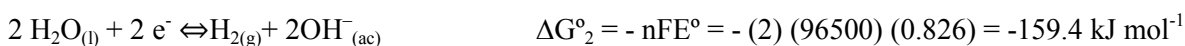
$$E = E^\circ_{(\text{Ti}^{3+}/\text{Ti}^+\text{-ENH})} + (0.059/2) \log [(\text{Ti}^{3+})/(\text{Ti}^+)], \text{ con } 2.303RT/nF = 0.059/2 \text{ y } \ln 10 = 2.303$$

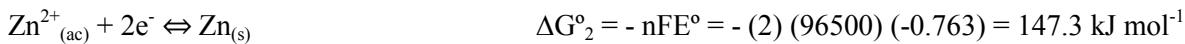
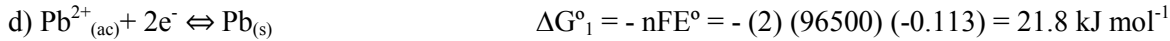
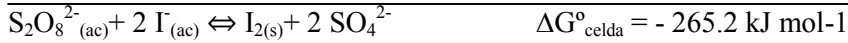
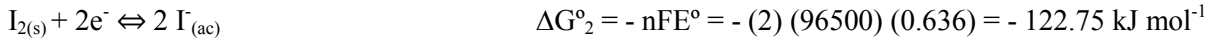
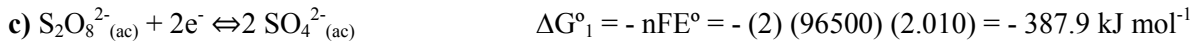
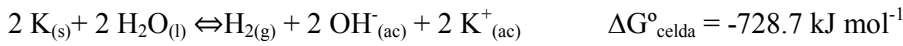
$$E = E^\circ_{(\text{Ti}^{3+}/\text{Ti}^+\text{-ENH})} + (0.059/2) \log [[\text{Ti}^{3+}]/[\text{Ti}^+]]$$



$$E = E^\circ_{(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}\text{-ENH})} + (0.059/6) \log [[\text{H}^+]^{14}[\text{Cr}_2\text{O}_7^{2-}] / [\text{Cr}^{3+}]^2]$$

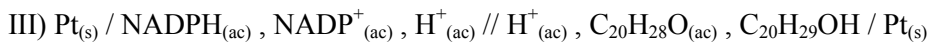
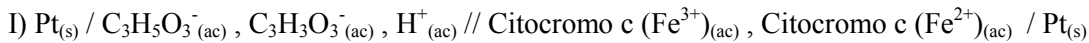
### Ejercicio 2





### Ejercicio 3

a)



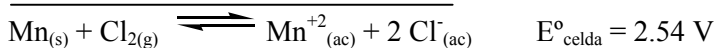
b)

I)  $\Delta G^\circ = -78.03 \text{ kJ/mol}$

II)  $\Delta G^\circ = -108.52 \text{ kJ/mol}$

III)  $\Delta G^\circ = -7.47 \text{ kJ/mol}$

### Ejercicio 4

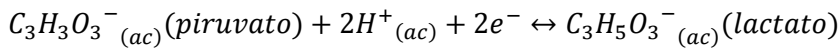
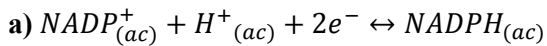


$E^\circ = 2.54 \text{ V} = E^\circ_{(\text{Cl}_2/\text{Cl}^- \text{-ENH})} - E^\circ_{(\text{Mn}^{2+}/\text{Mn-ENH})}$ ; entonces:

$E^\circ_{(\text{Mn}^{2+}/\text{Mn-ENH})} = - 2.54 + E^\circ_{(\text{Cl}_2/\text{Cl}^- \text{-ENH})}$ ; por lo que:

$E^\circ_{(\text{Mn}^{2+}/\text{Mn-ENH})} = - 1.18 \text{ V}$

### Ejercicio 5

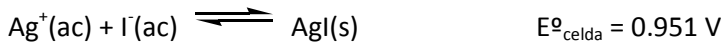
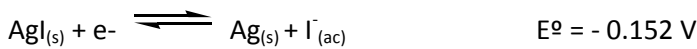


b)  $E^0 = -0.331 \text{ V}$

c)  $E = E^0 + \frac{RT}{2F} \ln \left( \frac{[NADP^+][C_3H_5O_3^{2-}]}{[NADPH][C_3H_3O_3^{2-}][H^+]}\right) = -0.117 \text{ V}$

d)  $\Delta G = -2 * 96500 * E = 22.62 \text{ kJmol}^{-1}$ , la reacción NO es espontánea.

### Ejercicio 6



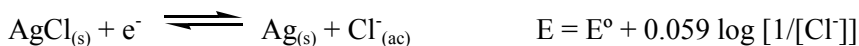
Como en el equilibrio  $\Delta G = 0$ , entonces  $E = 0$  por lo tanto  $E^0 = -(0.059/n) \log K$

y en este caso  $K = Kps$  (constante del producto de la solubilidad)

$E^0_{\text{celda}} = -0.059 \log Kps$  por lo que  **$Kps = 8 \times 10^{-17}$**

Por definición  $Kps = [Ag^+][I^-]$  entonces  **$s_{AgI} = 9 \times 10^{-9}$**

### Ejercicio 7

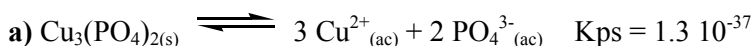


$E = 0.322 \text{ V} = E^0 + 0.059 \log \left[ \frac{(p_{H_2})^{1/2}}{[Cl^-][H^+]} \right]$  y como  $[H^+] = [Cl^-]$

$E = E^0 + 2(0.059)pH$

entonces el **pH = 0.83**

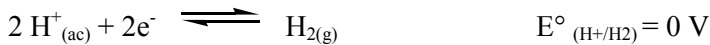
### Ejercicio 8



$Kps = 1.3 \cdot 10^{-37} = [3s]^3 [2s]^2 = 108 s^5$

Entonces  **$s(Cu_3(PO_4)_2_{(s)}) = (1.3 \cdot 10^{-37}/108)^{1/5} = 1.6 \times 10^{-8} \text{ M}$**





En el equilibrio  $E_{\text{celda}} = 0$ , entonces  $E^\circ_{\text{celda}} = - (0.059/6) \log 1/(\text{PO}_4^{3-})^2$

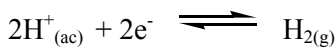
entonces  $E^\circ_{\text{celda}} = (0.059/3) \log[2 (1.6 \cdot 10^{-8})] = -0.147 \text{ V}$

### Ejercicio 9

Por definición, la función actividad es igual al producto del coeficiente de actividad y la concentración iónica expresada convenientemente. Para el caso de una concentración molal, la actividad se calcula en base molal, como  $a_i^m = \gamma_i^m m_i$ . En este caso, el supraíndice indica la base molal y el subíndice el tipo de ión. Para el caso de cambio de concentraciones;

$$a_1 = \gamma_1 m_1 = 0.930 (5.0 \cdot 10^{-3}) = 4.65 \cdot 10^{-3}$$

$$a_2 = \gamma_2 m_2 = 0.879 (20.0 \cdot 10^{-3}) = 17.58 \cdot 10^{-3}$$



$$E = E^\circ + (0.059/2) \log [(a_{\text{H}^+})^2 / p_{\text{H}_2}] \quad \text{y como } p_{\text{H}_2} = 1.15 \text{ atm}$$

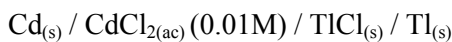
$$E = (0.059) \log (a_{\text{H}^+}) - 1.8 \cdot 10^{-3}$$

entonces :  $E_1 = -0.139 \text{ V}$

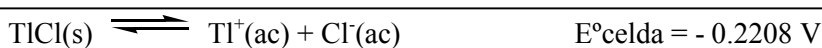
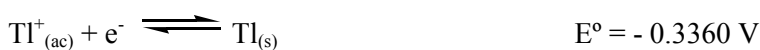
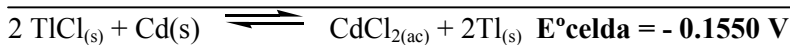
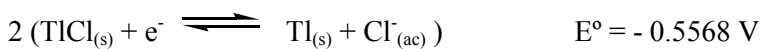
$$E_2 = -0.105 \text{ V}$$

por lo tanto:  $E_2 - E_1 = 0.034 \text{ V}$

### Ejercicio 10



$$T = 25^\circ\text{C} = 298 \text{ K}$$



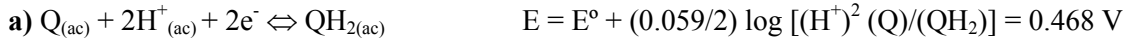
$$K_{\text{ps}} = [\text{Tl}^+] [\text{Cl}^-]$$

Como en el equilibrio  $E_{\text{celda}} = 0$ , entonces  $E^\circ_{\text{celda}} = -0.059 \log [1/K_{\text{ps}}]$

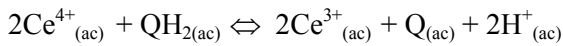
por lo que  $K_{ps} = 1.8 \times 10^{-4}$

### Problema 1

Pt / QH<sub>2</sub>, Q, (SAT), pH = 4 // CeCl<sub>4</sub> (0.01 M), CeCl<sub>3</sub> (0.02 M) / Pt



b) Considerando que la semicelda de la derecha es donde ocurre la reducción y la semicelda de la izquierda es aquella donde ocurre la oxidación, tenemos entonces que:



$E_{\text{celda}} = E_{\text{red}} - E_{\text{ox}} = E_{(Ce^{4+}/Ce^{3+})} - E_{(Q/QH_2)} = 0.954 \text{ V}$

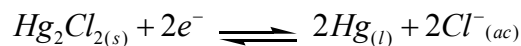
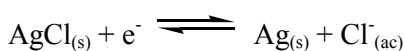
$\Delta G^\circ_{\text{celda}} = -nF E^\circ_{\text{celda}} = -2F[E^\circ_{(Ce^{4+}/Ce^{3+})} - E^\circ_{(Q/QH_2)}] = -142.029 \text{ kJ/mol}$

### Problema 2

a) Diagrama de la celda:

Pt<sub>(s)</sub> / Hg<sub>(l)</sub> / Hg<sub>2</sub>Cl<sub>2(s)</sub> / Cl<sup>-</sup><sub>(ac, sat)</sub> // Cl<sup>-</sup><sub>x(ac)</sub> / AgCl<sub>(s)</sub> / Ag<sub>(s)</sub>/Pt<sub>(s)</sub>

b) Reacciones:



c)  $E_{(AgCl/Ag-Hg_2Cl_2/Hg)} = E^\circ_{(AgCl/Ag)} - \frac{RT}{F} \ln [Cl^-]_x - E^\circ_{(Hg_2Cl_2/Hg)} + \frac{RT}{F} \ln [Cl^-]_{sat}$

$E_{(AgCl/Ag-Hg_2Cl_2/Hg)} = E^\circ_{\text{celda}} - \frac{RT}{F} \ln \left[ \frac{[Cl^-]_x}{[Cl^-]_{sat}} \right]$ , como  $[Cl^-]_{sat} = 1$

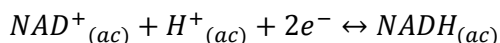
$E^\circ_{\text{celda}} = -0.02 \text{ V}$ ;  $T = 298 \text{ K}$ ,  $E_{(AgCl/Ag-Hg_2Cl_2/Hg)} = E^\circ_{\text{celda}} - \frac{RT}{F} \ln [Cl^-]_x$

$$E_{(AgCl/Ag-Hg_2Cl_2/Hg)} = E^{\circ}_{celda} - \frac{RT}{F} \ln [Cl^-]_x$$

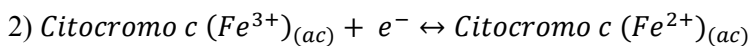
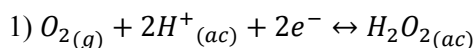
$$[Cl^-] = 3.03 \times 10^{-4} \text{ M}$$

### Problema 3

#### Oxidación:



#### Reducción:



#### a) Par 1

$$E'^{\circ} = E'^{\circ}(O_2/H_2O_2) - E'^{\circ}(NAD^+/NADH)$$

$$E'^{\circ} = 0.2741 \text{ V} - (-0.3327 \text{ V})$$

$$E'^{\circ} = 0.5968 \text{ V}$$

$$\Delta G'^{\circ} = -2 \times F \times E'^{\circ}$$

$$\Delta G'^{\circ} = -115.2 \text{ kJ/mol}$$

#### Par 2

$$E'^{\circ} = E'^{\circ}(\text{Cit}(Fe^{3+})/\text{Cit}(Fe^{2+})) - E'^{\circ}(NAD^+/NADH)$$

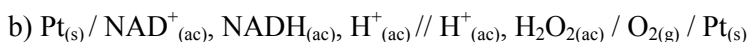
$$E'^{\circ} = 0.2223 \text{ V} - (-0.3327 \text{ V})$$

$$E'^{\circ} = 0.5450 \text{ V}$$

$$\Delta G'^{\circ} = -2 \times F \times E'^{\circ}$$

$$\Delta G'^{\circ} = -105.2 \text{ kJ/mol}$$

El par de reacciones más favorable termodinámicamente es el 1.



$$c) E'^{\circ} \text{ par 1} = 0.5672 \text{ V}, \Delta G'^{\circ} = -109.5 \text{ kJ/mol}$$

$$E'^{\circ} \text{ par 2} = 0.5746 \text{ V}, \Delta G'^{\circ} = -110.9 \text{ kJ/mol}$$

El par de reacciones 2 se vuelve más favorable a pH = 8.

### Problema 4

$$\mathbf{a)} \frac{\partial E^{\circ}}{\partial T} = 5.4 \times 10^{-4} \text{ V/K}$$

$$\Delta S^{\circ} = nF \left( \frac{\partial E^{\circ}}{\partial T} \right)$$

$$\Delta S^{\circ} = 52.1 \text{ J/mol K}$$

$$E^{\circ}(T2) = E(T1) + \left( \frac{\partial E}{\partial T} \right) \times (T2 - T1)$$

$$E^{\circ}(298) = E(293) + \left( \frac{\partial E}{\partial T} \right) \times (5K)$$

$$E^{\circ}(298 \text{ K}) = -0.2243 \text{ V}$$

$$\Delta G^{\circ}(298 \text{ K}) = -1 \times F \times E^{\circ}(298 \text{ K})$$

$$\Delta G^{\circ}(298 \text{ K}) = 21.64 \text{ kJ/mol}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ}$$

$$\Delta H^{\circ} = 37.17 \text{ kJ/mol}$$

$$\mathbf{b)} \Delta G^{\circ}(\text{citC} - \text{LP}) = -1 \times F \times (-0.214 \text{ V})$$

$$\Delta G^{\circ}(\text{citC} - \text{LP}) = 20.65 \text{ kJ/mol}$$

$$\Delta G^{\circ}(\text{citC}) = -1 \times F \times (-0.227 \text{ V})$$

$$\Delta G^{\circ}(\text{citC}) = 21.91 \text{ kJ/mol}$$

La unión de cardiolipina hace más favorable desde el punto de vista termodinámico la reducción de citocromo C.