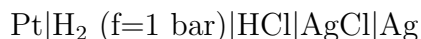


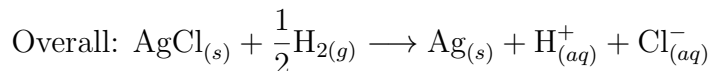
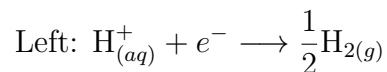
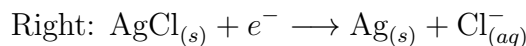
Chemistry 431
 Problem Set 13
 Fall 2023
 Solutions

1. For the cell



the measured *standard* EMF at 25.°C is $E^\ominus=0.222$ volts. If the measured EMF of the cell at 25.°C is 0.385 volts, what is the pH of the HCl solution? Using molalities, assume $\text{pH}=-\log_{10}(m_{\text{H}^+}/m_0)$.

Answer:



$$E = E^\ominus - \frac{RT}{F} \ln \frac{(m_{\text{H}^+}/m_0)(m_{\text{Cl}^-}/m_0)}{f_{\text{H}_2}^{1/2}}$$

$$0.385 \text{ V} = 0.222 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{96485 \text{ C mol}^{-1}} \ln(m_{\text{H}^+}/m_0)^2$$

$$(m_{\text{H}^+}/m_0)^2 = 1.75 \times 10^{-3}$$

$$m_{\text{H}^+}/m_0 = 0.0418$$

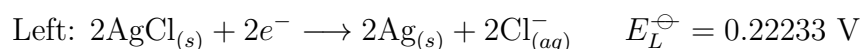
$$\text{pH} = -\log_{10}(0.0418) = 1.38$$

2. Consider the cell



(a) Use Table 11.1 to find the standard EMF for the cell at 25.°C.

Answer:



$$E^\ominus = E_R^\ominus - E_L^\ominus = 1.13594 \text{ V}$$

(b) Calculate ΔG at 25.°C when 1 Faraday of current passes through the cell.

Answer:

$$\Delta_{r,m}G^{\ominus} = -nFE^{\ominus}$$

For 1 Faraday, $n = 1$ and

$$\Delta_{r,m}G^{\ominus} = -(96485 \text{ C mol}^{-1})(1.13594 \text{ J C}^{-1}) = -109601 \text{ J}$$

(c) Show that the total reversible work attending the passage of 1 Faraday of current through the cell is

$$w_{rev} = -E^{\ominus}F + \frac{1}{2}RT.$$

Answer:

$$\begin{aligned} w_{rev} &= w_{elec} + w_{PV} \\ &= -E^{\ominus}F - P\Delta V \\ &= -E^{\ominus}F - \Delta(PV) \\ &= -E^{\ominus}F - \Delta(nRT) \\ &= -E^{\ominus}F - RT\Delta n_{gas} \\ \Delta n_{gas} &= -\frac{1}{2} \\ w_{rev} &= -E^{\ominus}F + \frac{1}{2}RT \end{aligned}$$

3. Show that

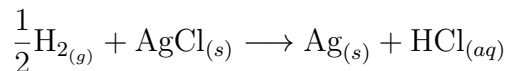
$$\left(\frac{\partial \frac{E^{\ominus}}{T}}{\partial T} \right)_P = \frac{\Delta_m H^{\ominus}}{nFT^2}$$

Answer:

$$\begin{aligned} \left(\frac{\partial E^{\ominus}/T}{\partial T} \right)_P &= -\frac{1}{nF} \left(\frac{\partial \Delta_{r,m}G^{\ominus}/T}{\partial T} \right)_P \\ &= \frac{\Delta_{r,m}H^{\ominus}}{nFT^2} \end{aligned}$$

by the Gibbs-Helmholtz equation.

4. When the reaction



takes place at 25.°C in a cell, the reversible electrical work done by the reaction on the surroundings is 34476 Joules. When the same reaction takes place in a calorimeter doing only PV -work at a constant pressure of 1 bar at 25.°C, the heat transferred to the surroundings is 39292 Joules (the reaction is exothermic).

- (a) What is the heat liberated by the reversible reaction to the surroundings in the electrochemical cell?

Answer:

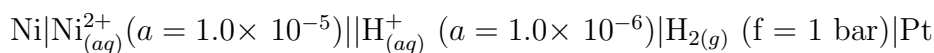
$$\begin{aligned}
 \Delta U &= q + w \\
 &= -39292 \text{ J} - P\Delta V \\
 &= -39292 \text{ J} - RT\Delta n_{gas} \\
 &= -39292 \text{ J} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(-0.5 \text{ mol}) = -38053 \text{ J} \\
 -38053 \text{ J} &= q_{rev} + \frac{1}{2}(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) - 34476 \text{ J} \\
 q_{rev} &= -4816 \text{ J}
 \end{aligned}$$

- (b) Calculate $\Delta_m S^\ominus$, $\Delta_m H^\ominus$ and $\Delta_m U^\ominus$ for the reaction. Assume ΔV for the reaction is just that associated with the disappearance of 1/2 mole of an ideal gas.

Answer:

$$\begin{aligned}
 \Delta_{r,m} U^\ominus &= -38053 \text{ J mol}^{-1} \\
 \Delta_{r,m} H^\ominus &= q = -39292 \text{ J mol}^{-1} \\
 \Delta_{r,m} G^\ominus &= w_{elec} = -34476 \text{ J} \\
 \Delta_{r,m} S^\ominus &= \frac{\Delta_{r,m} H^\ominus - \Delta_{r,m} G^\ominus}{T} \\
 &= \frac{-39292 \text{ J mol}^{-1} + 34476 \text{ J mol}^{-1}}{298 \text{ K}} = -16.16 \text{ J mol}^{-1}\text{K}^{-1}
 \end{aligned}$$

5. Use Table 11.1 to calculate the EMF of the cell

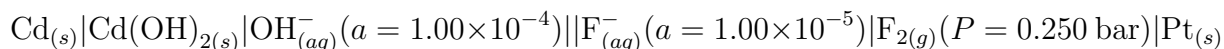


at 25.°C.

Answer:

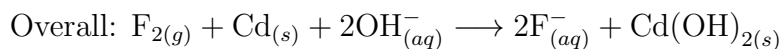
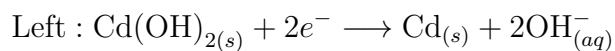
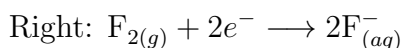
$$\begin{aligned}
 \text{Right: } &2\text{H}_{(aq)}^+ + 2e^- \longrightarrow \text{H}_{2(g)} \\
 \text{Left: } &\text{Ni}_{2(aq)}^{2+} + 2e^- \longrightarrow \text{Ni}_{(s)} \\
 \text{Overall: } &2\text{H}_{(aq)}^+ + \text{Ni}_{(s)} \longrightarrow \text{H}_{2(g)} + \text{Ni}_{(aq)}^{2+} \\
 E^\ominus &= E_R^\ominus - E_L^\ominus = 0 - (-0.257 \text{ V}) = 0.257 \text{ V} \\
 E &= E^\ominus - \frac{RT}{nF} \ln Q \\
 E &= E^\ominus - \frac{RT}{nF} \ln \frac{a_{\text{Ni}^{2+}} f(\text{H}_{2(g)})}{(a_{\text{H}^+})^2} \\
 &= 0.257 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln \frac{10^{-5} \times 1}{(10^{-6})^2} = 0.050 \text{ V}
 \end{aligned}$$

6. At 298 K, the EMF of the electrochemical cell



is 3.716 V. Given the standard half-cell reduction potentials $E_{\text{Cd}^{2+}/\text{Cd}(\text{OH})_2/\text{Cd}}^\ominus = -0.809$ V and $E_{\text{F}^-/\text{F}_2}^\ominus = 2.866$ V, calculate the fugacity coefficient for the fluorine gas in the cell.

Answer:



$$Q = \frac{(a_{\text{F}^-})^2}{(a_{\text{OH}^-})^2 P_{\text{F}_2} \gamma / P^\ominus}$$

$$E^\ominus = E_R^\ominus - E_L^\ominus = 3.675 \text{ V}$$

$$E = E^\ominus - \frac{RT}{nF} \ln Q = E^\ominus - \frac{RT}{nF} \ln \frac{(a_{\text{F}^-})^2}{(a_{\text{OH}^-})^2 P_{\text{F}_2} \gamma / P^\ominus}$$

$$3.716 \text{ V} = 3.675 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln \frac{(1.00 \times 10^{-5})^2}{(1.00 \times 10^{-4})^2 (0.250 \gamma)}$$

$$\gamma = 0.975$$