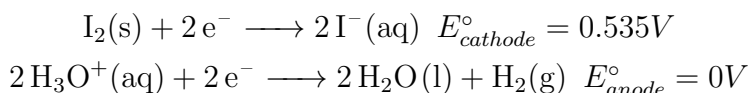


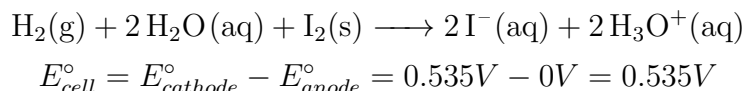
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Problem 17.31. An $\text{I}_2(\text{s}) \mid \text{I}^- (1.00 \text{ M})$ half-cell is connected to an $\text{H}_3\text{O}^+ \mid \text{H}_2 (1 \text{ atm})$ half-cell in which the concentration of the hydronium ion is unknown. The measured cell potential is 0.841 V, and the $\text{I}_2 \mid \text{I}^-$ half-cell is the cathode. What is the pH in the $\text{H}_3\text{O}^+ \mid \text{H}_2$ half-cell?

Solution: The standard reduction potential of the cathode and the anode are



So the standard cell potential is

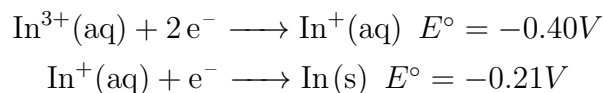


According to the Nernst Equation,

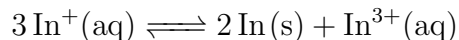
$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0592\text{V}}{n} \log_{10} \frac{[\text{I}^-]^2 [\text{H}_3\text{O}^+]^2}{P_{\text{H}_2}} \\ \implies 0.841\text{V} &= 0.535\text{V} - \frac{0.0592\text{V}}{2} \log_{10} \frac{1.00^2 \times [\text{H}_3\text{O}^+]^2}{1} \\ \implies pH &= -\log_{10}[\text{H}_3\text{O}^+] = \underline{5.17}\end{aligned}$$

□

Problem 17.37. The following standard reduction potentials have been determined for the aqueous chemistry of indium:



Calculate the equilibrium constant (K) for the disproportionation of $\text{In}^+(\text{aq})$ at 25°C.



Solution: The standard reduction potential of the disproportionation reaction is

$$E_3^\circ = E_2^\circ - E_1^\circ = -0.21\text{V} - (-0.40\text{V}) = 0.19\text{V}$$

The equilibrium constant for the disproportionation reaction is

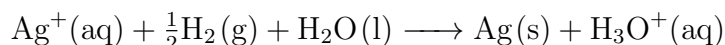
$$\begin{aligned}\log_{10} K &= \frac{n}{0.0592\text{V}} E_3^\circ = \frac{2}{0.0592\text{V}} \times 0.19\text{V} \\ \implies K &= \underline{2.6 \times 10^6}\end{aligned}$$

□

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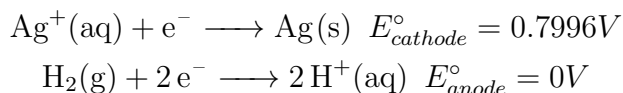
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Problem 17.40. In a galvanic cell, the cathode consists of a $\text{Ag}^+(1.00\text{ M})|\text{Ag}$ half-cell. The anode is a platinum wire, with hydrogen bubbling over it at 1.00-atm pressure, which is immersed in a buffer solution containing benzoic acid and sodium benzoate. The concentration of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is 0.10 M, and that of benzoate ion ($\text{C}_6\text{H}_5\text{COO}^-$) is 0.050 M. The overall cell reaction is then



and the measured cell potential is 1.030 V. Calculate the pH in the buffer solution and determine the K_a of benzoic acid.

Solution: The standard reduction potential of the half-cell reaction are



So the standard cell potential is

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.7996\text{V} - 0\text{V} = 0.7996\text{V}$$

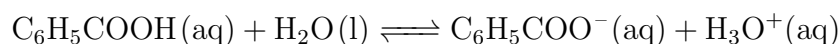
According to the Nernst Equation,

$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0592\text{V}}{n} \log_{10} \frac{[\text{H}_3\text{O}^+]}{[\text{Ag}^+]P_{\text{H}_2}} \\ \implies 1.030\text{V} &= 0.7996\text{V} - \frac{0.0592\text{V}}{1} \frac{[\text{H}_3\text{O}^+]}{1.00 \times 1.00} \\ \implies \text{pH} &= -\log_{10}[\text{H}_3\text{O}^+] = \underline{3.89}\end{aligned}$$

So the concentration of H_3O^+ is

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.89} \text{mol} \cdot \text{L}^{-1} = 1.28 \times 10^{-4} \text{mol} \cdot \text{L}^{-1}$$

The ionization equation of benzoic is



So the K_a of benzoic is

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{0.050 \times 1.28 \times 10^{-4}}{0.10} = \underline{6.4 \times 10^{-5}}$$

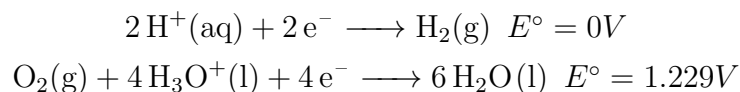
□

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Problem 17.47. Would CdS be a suitable semiconductor for direct photo-electrochemical water splitting? Why or why not? The conduction band lies at about -1.25 V vs NHE and the valence band lies at about 0.12 V vs NHE.

Solution: No.

Because the standard reduction potential of $\text{H}_2|\text{H}^+$ and $\text{O}_2|\text{H}_2\text{O}$ are



Reason: the conduction band of CdS is below the 0 V , so it is sufficient to reduce H^+ to H_2 , but the valence band of CdS is not over 1.229 V , so it can not oxidize H_2O to O_2 . □

Problem 17.54. (a) What quantity of charge (in coulombs) is a fully charged 1.34-V zinc-mercuric oxide watch battery theoretically capable of furnishing if the mass of HgO in the battery is 0.50 g ?

(b) What is the theoretical maximum amount of work (in joules) that can be obtained from this battery?

Solution:

(a) The number of moles of HgO is

$$n(\text{HgO}) = \frac{m(\text{HgO})}{M(\text{HgO})} = \frac{0.50\text{g}}{216.59\text{g} \cdot \text{mol}^{-1}} = 2.3 \times 10^{-3}\text{mol}$$

Each mole of HgO corresponds to 2 mol electrons transferred, so the quantity of charge that the zinc-mercuric oxide watch battery is theoretically capable of furnishing is

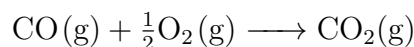
$$Q = 2n(\text{HgO})F = 2 \times 2.3 \times 10^{-3}\text{mol} \times 96485\text{C} \cdot \text{mol}^{-1} = \underline{4.5 \times 10^2\text{C}}$$

(b) The theoretical maximum amount of work (in joules) that can be obtained from this battery is

$$w = QV = 4.5 \times 10^2\text{C} \times 1.34\text{V} = \underline{6.0 \times 10^2\text{J}}$$

□

Problem 17.58. Consider the fuel cell that accomplishes the overall reaction



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Calculate the maximum electrical work that could be obtained from the conversion of 1.00 mol of CO(g) to CO₂(g) in such a fuel cell operated with 100% efficiency at 25°C and with the pressure of each gas equal to 1 atm.

Solution: The standard free energy change of the reaction are

$$\begin{aligned}\Delta G_f^\circ &= \Delta G_f^\circ(C_2O) - \Delta G_f^\circ(CO) - \frac{1}{2}\Delta G_f^\circ(O_2) \\ &= -394.36 \text{ kJ} \cdot \text{mol}^{-1} - (-137.15 \text{ kJ} \cdot \text{mol}^{-1}) - \frac{1}{2} \times 0 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -257.21 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

So the maximum electrical work that could be obtained from the fuel cell at is

$$w = -n\Delta G_f^\circ\eta = -1.00 \text{ mol} \times (-257.21 \text{ kJ} \cdot \text{mol}^{-1}) \times 100\% = \underline{257.21 \text{ kJ}}$$

□

Problem 17.66. A current of 75,000 A is passed through an electrolysis cell containing molten MgCl₂ for 7.0 days. Calculate the maximum theoretical mass of magnesium that can be recovered.

Solution: The number of moles of electrons transferred in 7.0 days is

$$n = \frac{it}{F} = \frac{75000 \text{ A} \times 7.0 \times 24 \times 60 \times 60 \text{ s}}{96485 \text{ C} \cdot \text{mol}^{-1}} = 4.7 \times 10^5 \text{ mol}$$

Each mole of magnesium corresponds to 2 mol electrons transferred, so the maximum theoretical mass of magnesium that can be recovered is

$$m(\text{Mg}) = M(\text{Mg})\frac{n}{2} = 24.3 \text{ g} \cdot \text{mol}^{-1} \times \frac{4.7 \times 10^5 \text{ mol}}{2} = 5.7 \times 10^6 \text{ g} = \underline{5.7 \text{ t}}$$

□

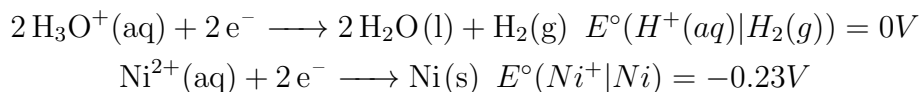
Problem 17.71. An electrolytic cell consists of a pair of inert metallic electrodes in a solution buffered to pH= 5.0 and containing nickel sulfate (NiSO₄) at a concentration of 1.00 M. A current of 2.00 A is passed through the cell for 10.0 hours.

- What product is formed at the cathode?
- What is the mass of this product?
- If the pH is changed to pH= 1.0, what product will form at the cathode?

Solution:

- The standard reduction potential of H⁺(aq)|H₂(g) and Ni²⁺|Ni(s) are

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According to the Nernst Equation, the reduction potential of $\text{H}^+(\text{aq})|\text{H}_2(\text{g})$ and $\text{Ni}^{2+}|\text{Ni}(\text{s})$ are

$$\begin{aligned} E(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) &= E^\circ(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) - \frac{0.0592\text{V}}{n} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}_3\text{O}^+]^2} \\ &= 0\text{V} - \frac{0.0592\text{V}}{2} \log_{10} \frac{1}{(10^{-5.0})^2} \\ &= -0.296\text{V} \\ E(\text{Ni}^{2+}|\text{Ni}) &= E^\circ(\text{Ni}^{2+}|\text{Ni}) - \frac{0.0592\text{V}}{n} \log_{10} \frac{1}{[\text{Ni}^{2+}]} \\ &= -0.23\text{V} - \frac{0.0592\text{V}}{2} \log_{10} \frac{1}{1.00} \\ &= -0.23\text{V} \end{aligned}$$

Because $E(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) < E(\text{Ni}^{2+}|\text{Ni})$, the product formed at the cathode is Ni.

(b) The number of moles of electrons transferred in 10.0 hours is

$$n = \frac{it}{F} = \frac{2.00\text{A} \times 60 \times 60 \times 10.0\text{s}}{96485\text{C} \cdot \text{mol}^{-1}} = 0.746\text{mol}$$

Each mole of Ni corresponds to 2 mol electrons transferred, so the mass of Ni produced is

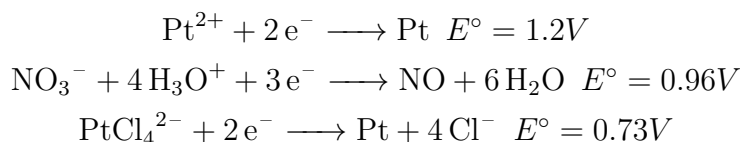
$$m(\text{Ni}) = M(\text{Ni}) \frac{n}{2} = 58.69\text{g} \cdot \text{mol}^{-1} \times \frac{0.746\text{mol}}{2} = \underline{21.9\text{g}}$$

(c) When pH= 1, the reduction potential of $\text{H}^+(\text{aq})|\text{H}_2(\text{g})$ is

$$\begin{aligned} E(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) &= E^\circ(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) - \frac{0.0592\text{V}}{n} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}_3\text{O}^+]^2} \\ &= 0\text{V} - \frac{0.0592\text{V}}{2} \log_{10} \frac{1}{(10^{-1.0})^2} \\ &= -0.0592\text{V} \end{aligned}$$

Because $E(\text{H}^+(\text{aq})|\text{H}_2(\text{g})) > E(\text{Ni}^{2+}|\text{Ni})$, the product formed at the cathode is H₂. □

Problem 17.84. By considering these half-reactions and their standard reduction potentials,

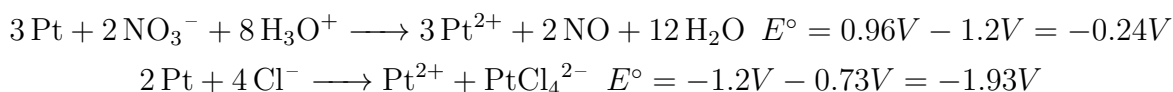


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account for the fact that platinum will dissolve in a mixture of hydrochloric acid and nitric acid (aqua regia) but will not dissolve in either acid alone.

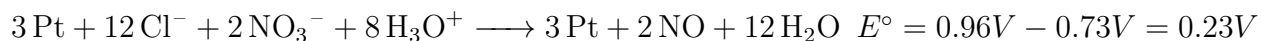
Solution: The standard potential of the reaction in which platinum dissolves in hydrochloric acid and nitric acid respectively are



so their Gibbs free energy are both positive

$$\begin{aligned} 3\text{Pt} + 2\text{NO}_3^- + 8\text{H}_3\text{O}^+ &\longrightarrow 3\text{Pt}^{2+} + 2\text{NO} + 12\text{H}_2\text{O} \\ \Delta G_f^\circ = -nFE^\circ &= -6\text{mol} \times 96485\text{C} \cdot \text{mol} \times (-0.24\text{V}) = 1.4 \times 10^5\text{J} > 0 \\ 2\text{Pt} + 4\text{Cl}^- &\longrightarrow \text{Pt}^{2+} + \text{PtCl}_4^{2-} \\ \Delta G_f^\circ = -nFE^\circ &= -2\text{mol} \times 96485\text{C} \cdot \text{mol} \times (-1.93\text{V}) = 3.7 \times 10^5\text{J} > 0 \end{aligned}$$

However, the standard potential of the reaction in which platinum dissolves in a mixture of hydrochloric acid and nitric acid is



and its Gibbs free energy is negative

$$\begin{aligned} 3\text{Pt} + 12\text{Cl}^- + 2\text{NO}_3^- + 8\text{H}_3\text{O}^+ &\longrightarrow 3\text{PtCl}_4^{2-} + 2\text{NO} + 12\text{H}_2\text{O} \\ \Delta G_f^\circ = -nFE^\circ &= -6\text{mol} \times 96485\text{C} \cdot \text{mol} \times 0.23\text{V} = -1.3 \times 10^5\text{J} < 0 \end{aligned}$$

Therefore, platinum will dissolve in a mixture of hydrochloric acid and nitric acid (aqua regia) but will not dissolve in either acid alone. \square