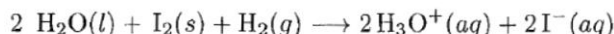


Answers to HW 8#

- 17.31** The $\text{I}_2|\text{I}^-$ half-reaction is at the cathode, the site of reduction. Hence the $\text{H}_3\text{O}^+|\text{H}_2$ half-reaction is an oxidation (at the anode). The overall reaction is



Assume that the temperature is 25°C and use the data in text Appendix E to obtain $\mathcal{E}_{\text{cell}}^\circ$ of the cell. The appropriate standard reduction potentials are combined as follows

$$\mathcal{E}_{\text{cell}}^\circ = \mathcal{E}_{\text{cathode}}^\circ - \mathcal{E}_{\text{anode}}^\circ = 0.535 (\text{I}_2|\text{I}^-) - (0.000) (\text{H}_3\text{O}^+|\text{H}_2) = 0.535 \text{ V}$$

The measured cell voltage depends on the concentrations and partial pressures of reactants and products according to the Nernst equation. At 25°C

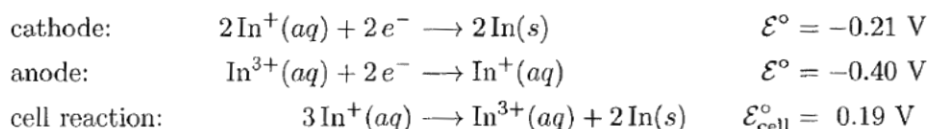
$$0.841 \text{ V} = 0.535 \text{ V} - \left(\frac{0.0592 \text{ V}}{2} \right) \log \left(\frac{[\text{H}_3\text{O}^+]^2 [\text{I}^-]^2}{P_{\text{H}_2}} \right)$$

The concentration of the iodide ion $[\text{I}^-]$ equals 1.00 M ; the partial pressure of hydrogen P_{H_2} equals 1 atm . Substitution gives

$$(0.841 - 0.535) \text{ V} = -\frac{0.0592 \text{ V}}{2} \log \left(\frac{[\text{H}_3\text{O}^+]^2 (1.00)^2}{1.00} \right)$$

The unit V (for volts) cancels out. Solving for $\log[\text{H}_3\text{O}^+]$ gives -5.17 . The pH equals $-\log[\text{H}_3\text{O}^+]$, so it is 5.17.

- 17.37** In a disproportionation reaction, a single species is simultaneously oxidized and reduced. Here, some In^+ ion is oxidized to In^{3+} ion while some is reduced to elemental In. Calculate $\mathcal{E}_{\text{cell}}^\circ$, the standard potential that would be observed if the reaction took place in an electrochemical cell. Use standard reduction potentials from text Appendix E. They apply exactly because the temperature is 298 K



Now get the value of K

$$\ln K = \frac{nF\mathcal{E}_{\text{cell}}^\circ}{RT} = \frac{2(9.6485 \times 10^4 \text{ C mol}^{-1})(0.19 \text{ V})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 15 \quad K = e^{15} = \boxed{3 \times 10^6}$$

17.40 Figure the standard potential difference for the reaction

$$\Delta\mathcal{E}^\circ = \mathcal{E}^\circ(\text{Ag}^+|\text{Ag}) - \mathcal{E}^\circ(\text{H}_3\text{O}^+|\text{H}_2) = 0.7996 - (0) = 0.7996 \text{ V}$$

Write the Nernst equation at 25°C

$$\Delta\mathcal{E} = \Delta\mathcal{E}^\circ - \frac{0.0592}{n} \log \frac{[\text{H}_3\text{O}^+]}{[\text{Ag}^+]P_{\text{H}_2}^{1/2}}$$

and substitute all of the known values

$$1.030 = 0.7996 - \frac{0.0592}{1} \log \frac{[\text{H}_3\text{O}^+]}{(1.00)(1.00)}$$

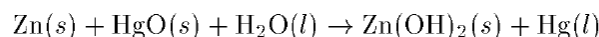
From this equation, $[\text{H}_3\text{O}^+]$ is 1.28×10^{-4} M. The pH in the buffer solution in the cell is 3.89. Now, compute the K_a of the benzoic acid by substitution in the acid ionization equilibrium expression

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

17.47 Use text Figure 17.19. The potential of the conduction band (labelled CB in the figure) must be more negative than 0 V in order to provide electrons to reduce H^+ ions to H_2 . Also, the potential of the valence band must be more positive than 1.229 V to accept electrons from the oxidation of H_2O to O_2 . The VB potential in CdS is not sufficiently positive to oxidize water; the answer is **no**.

17.54

a) The cell reaction is



The reduction of 1 mol of HgO occurs with the passage of 2 mol of electrons through an outside circuit, that is, $\text{Hg}(\text{II})$ is reduced to $\text{Hg}(0)$. 0.50 g of HgO ($\mathcal{M} = 216.59 \text{ g mol}^{-1}$) is 2.3×10^{-3} mol. Hence, 4.6×10^{-3} mol of electrons must pass the circuit to cause complete discharge. Multiplying by the Faraday constant converts this to $4.5 \times 10^2 \text{ C}$.

b) The maximum electrical work performed on the battery is

$$w = -Q\Delta\mathcal{E} = -(4.5 \times 10^2 \text{ C})(1.34 \text{ V}) = -6.0 \times 10^2 \text{ J}$$

The battery can perform at most 600 J of electrical work on its surroundings.

17.58

The ΔG° for the oxidation of 1.00 mol of $\text{CO}(g)$ to $\text{CO}_2(g)$ is -257.21 kJ , regardless of how the reaction is performed. If the reaction is performed with 100% efficiency at standard conditions, then $\Delta G^\circ = w$ and the cell absorbs -257.21 kJ of work, that is, 257.21 kJ of work is obtained.

17.66

7.0 days is $6.048 \times 10^5 \text{ s}$. A steady current of 75 000 A for this period means that $4.536 \times 10^{10} \text{ C}$ passes through the circuit. Dividing by the Faraday constant gives the chemical amount of electrons passing through the circuit. It is $4.70 \times 10^5 \text{ mol}$. Every 2 mol of electrons theoretically accounts for the deposition of 1 mol of Mg. The theoretical yield of Mg is therefore $2.35 \times 10^5 \text{ mol}$, which is $5.7 \times 10^6 \text{ g}$.

- 17.71** a) The product at the cathode could be either gaseous hydrogen from the reduction of $1.0 \times 10^{-5} \text{ M H}_3\text{O}^+(aq)$ or metallic nickel from the reduction of $1.00 \text{ M Ni}^{2+}(aq)$. Direct observation of an operating cell could settle the issue at a glance.¹ In this cell, at 25°C , the potential for the reduction of $\text{Ni}^{2+}(aq)$ to $\text{Ni}(s)$ is -0.23 V , as tabulated in text Appendix E, because the concentration of the Ni^{2+} ion is 1 M . The reduction potential for $\text{H}_3\text{O}^+(aq)$ to $\text{H}_2(g)$ is not equal to its tabulated value of 0.00 V because the concentration of H_3O^+ ion is $1.0 \times 10^{-5} \text{ M}$ and not the standard 1 M . Use the Nernst equation to figure the $\text{H}_3\text{O}^+(aq) | \text{H}_2(g)$ reduction potential under this circumstance. Assume that the cell operates at 25°C

$$\mathcal{E}_{\text{H}_3\text{O}^+(aq) | \text{H}_2(g)} = \mathcal{E}^\circ - \frac{0.0592 \text{ V}}{1} \log \left(\frac{P_{\text{H}_2}^{1/2}}{[\text{H}_3\text{O}^+]} \right) = 0.0 - (0.0592 \text{ V}) \log \left(\frac{1}{10^{-5}} \right) = -0.296 \text{ V}$$

This result is algebraically less than the -0.23 V for $\text{Ni}^{2+}(aq) | \text{Ni}(s)$. Therefore nickel forms first.

- b) A current of 2.00 amperes for 10 hours is a current of 2.00 C s^{-1} for 36000 s . Therefore $7.20 \times 10^4 \text{ C}$ passes through the cell. The mass of Ni deposited is

$$m_{\text{Ni}} = 7.20 \times 10^4 \text{ C} \times \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Ni}(s)}{2 \text{ mol } e^-} \right) \left(\frac{58.69 \text{ g Ni}}{1 \text{ mol Ni}} \right) = \boxed{21.9 \text{ g Ni}}$$

The volume of the electrolyte has to be so large that removal of 21.9 g of nickel does not lower the concentration of $\text{Ni}^{2+}(aq)$ ion to the point that H_3O^+ ion starts to be reduced.

- c) If the pH is 1.0 , then $[\text{H}_3\text{O}^+]$ is 0.10 M . The Nernst equation for the reduction of H_3O^+ to $\text{H}_2(g)$ at 1 atm and 25°C becomes

$$\mathcal{E} = 0.00 - 0.0592 \text{ V} \log \left(\frac{1.00}{1 \times 10^{-1}} \right) = -0.0592 \text{ V}$$

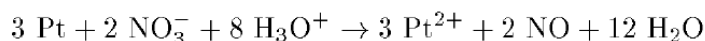
At this pH, $\text{H}_2(g)$ rather than $\text{Ni}(s)$ tends to form at the cathode.

17.84

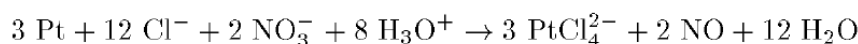
In the absence of hydrochloric acid, the $\Delta\mathcal{E}^\circ$ for the oxidation of Pt by nitric acid is

$$\Delta\mathcal{E}^\circ = 0.96 - 1.2 \text{ V} = -0.24 \text{ V} < 0$$

The negative sign shows that the reaction



is not spontaneous. When hydrochloric acid is present (as with aqua regia) the Pt^{2+} can complex with chloride ion. For the reaction



the cell voltage is $\Delta\mathcal{E}^\circ = 0.96 - 0.73 = 0.23 \text{ V} > 0$; the reaction can occur spontaneously.