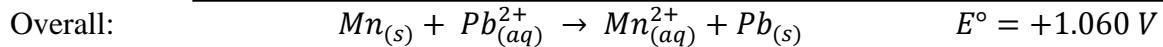
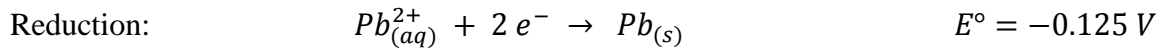
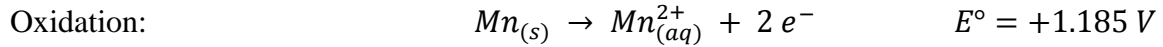


Answers to Exercise 9.5

Nonstandard Potential for Electrochemical Cells: The Nernst Equation!

1. **Step 1: Find v_e and E° by balancing redox equation**



Therefore, $v_e = 2$

Step 2: Determine activities for all reactants and products

$$a_{\text{Mn}_{(s)}} = 1$$

$$a_{\text{Mn}_{(aq)}^{2+}} = \frac{0.0375 \text{ M}}{1 \text{ M}} = 0.0375$$

$$a_{\text{Pb}_{(aq)}^{2+}} = \frac{0.0125 \text{ M}}{1 \text{ M}} = 0.0125$$

$$a_{\text{Pb}_{(s)}} = 1$$

Step 3: Calculate reaction quotient

$$Q = \frac{(a_{\text{Mn}_{(aq)}^{2+}})(a_{\text{Pb}_{(s)}})}{(a_{\text{Mn}_{(s)}})(a_{\text{Pb}_{(aq)}^{2+}})} = \frac{(0.0375)(1)}{(1)(0.0125)} = 3.00$$

Step 4: Calculate potential for reaction under nonstandard conditions

$$E = E^\circ - \frac{RT}{v_e F} \ln Q$$

$$E = (1.060 \text{ V}) - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(96485 \frac{\text{C}}{\text{mol}})} \ln(3.00) \times \frac{1 \text{ V}}{1 \frac{\text{J}}{\text{C}}}$$

$$E = 1.060 \text{ V} - 0.014 \text{ V}$$

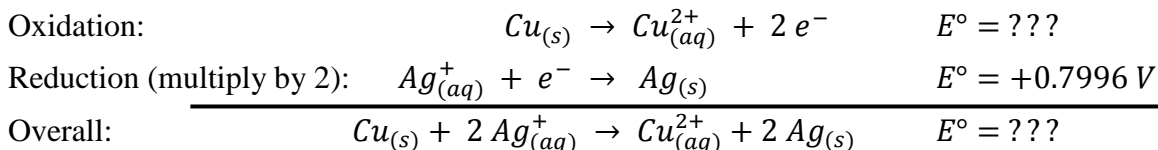
$$E = 1.046 \text{ V}$$

Step 5: Check your work

Does your answer seem reasonable?

2. This question requires you to work backward through the same process as in question 1. So, start with cell potential. Use it and reaction quotient to calculate standard potential. Then use standard potential to calculate the standard reduction potential of $\text{Cu}_{(aq)}^{2+}$.

Step 1: Find v_e by balancing redox equation



Therefore, $v_e = 2$

Step 2: Determine activities for all reactants and products

$$\begin{array}{ll} a_{\text{Cu}_{(s)}} = 1 & a_{\text{Cu}_{(aq)}^{2+}} = \frac{0.067 \text{ M}}{1 \text{ M}} = 0.067 \\ a_{\text{Ag}_{(aq)}^{+}} = \frac{0.0084 \text{ M}}{1 \text{ M}} = 0.0084 & a_{\text{Ag}_{(s)}} = 1 \end{array}$$

Step 3: Calculate reaction quotient

$$Q = \frac{(a_{\text{Cu}_{(aq)}^{2+}})(a_{\text{Ag}_{(s)}})^2}{(a_{\text{Cu}_{(s)}})(a_{\text{Ag}_{(aq)}^{+}})^2} = \frac{(0.067)(1)^2}{(1)(0.0084)^2} = 9.5 \times 10^2$$

Step 4: Calculate standard potential for reaction

$$E = E^{\circ} - \frac{RT}{v_e F} \ln Q$$

$$E^{\circ} = E + \frac{RT}{v_e F} \ln Q$$

$$E^{\circ} = (0.3696 \text{ V}) + \frac{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298.15 \text{ K})}{(2)(96485 \frac{\text{C}}{\text{mol}})} \ln(9.5 \times 10^2) \times \frac{1 \text{ V}}{1 \text{ C}}$$

$$E^{\circ} = 0.3696 \text{ V} + 0.088 \text{ V}$$

$$E^{\circ} = 0.4577 \text{ V}$$

Step 5: Calculate standard half-cell potential for oxidation of Cu to Cu^{2+}

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation half-cell}} + E^{\circ}_{\text{reduction half-cell}}$$

$$E^{\circ}_{\text{oxidation half-cell}} = E^{\circ}_{\text{cell}} - E^{\circ}_{\text{reduction half-cell}}$$

$$E^{\circ}_{\text{oxidation half-cell}} = (0.4577 \text{ V}) - (0.7996 \text{ V})$$

$$E^{\circ}_{\text{oxidation half-cell}} = -0.3419 \text{ V}$$

Step 6: Calculate standard reduction potential for Cu^{2+} to Cu

This is the reverse of the observed half-reaction, so multiply by -1

$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = -(-0.3419 \text{ V}) = +0.3419$$

Step 7: Check your work

Does your answer seem reasonable?

Most standard reduction potentials fall between +3 V and -3 V; the calculated value falls within that range. Reference tables give values of approximately +0.34 V for the standard reduction potential of Cu^{2+} .

3.

- (a) Since there is no net reaction, the standard potential for this cell must be zero.

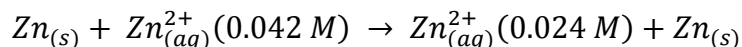
This is what is called a “concentration cell”. The driving force for the reaction is the fact that the concentrations in the two half-cells are different.

- (b) Positive.

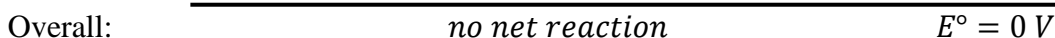
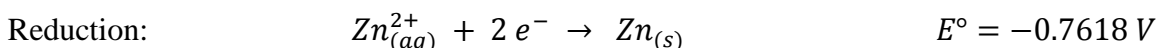
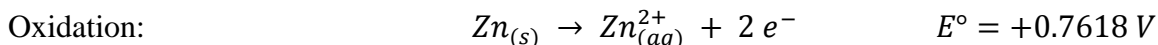
A positive cell potential indicates a reaction that is product-favoured.

A concentration cell reaches equilibrium when the concentrations in the two half-cells become the same. In the cell as written, the concentration of Zn^{2+} in the reduction half-cell (the righthand side in cell notation) is higher than the concentration of Zn^{2+} in the oxidation half-cell (the lefthand side in cell notation). Thus, reduction of some Zn^{2+} to Zn in the reduction half-cell and oxidation of some Zn to Zn^{2+} in the oxidation half-cell will bring the two solution concentrations closer together.

Essentially, the following reaction is product-favoured:



- (c) **Step 1: Find v_e and E° by balancing redox equation**



Therefore, $v_e = 2$

Step 2: Determine activities for all reactants and products

$$a_{Zn_{(s)}} = 1 \quad \quad \quad a_{Zn_{(aq)}^{2+}} = \frac{0.024 M}{1 M} = 0.024$$

$$a_{Zn_{(aq)}^{2+}} = \frac{0.042 M}{1 M} = 0.042 \quad \quad \quad a_{Zn_{(s)}} = 1$$

Step 3: Calculate reaction quotient

$$Q = \frac{(a_{Zn_{(aq)}^{2+}})(a_{Zn_{(s)}})}{(a_{Zn_{(s)}})(a_{Zn_{(aq)}^{2+}})} = \frac{(0.024)(1)}{(1)(0.042)} = 0.57$$

Step 4: Calculate potential for reaction under nonstandard conditions

$$E = E^\circ - \frac{RT}{v_e F} \ln Q$$

$$E = (0 V) - \frac{(8.314 \frac{J}{mol \cdot K})(298.15 K)}{(2)(96485 \frac{C}{mol})} \ln(0.57) \times \frac{1 V}{1 \frac{J}{C}}$$

$$E = 0 V - (-0.0072 V)$$

$$E = +0.0072 V$$

Step 5: Check your work

Does your answer seem reasonable?

It is consistent with the prediction from part (b) and has a reasonable order of magnitude.