

Chapter 9

Electrochemistry

1. **What is a passive electrode? What quality in a metal is required to serve as a passive electrode? Give three examples of metals that would make good passive electrodes.**

A passive electrode is an electrode that does not participate in the reaction. Passive electrodes are inert metals that serve as the surface on which electrons are transferred between the external circuit and the media (often an aqueous solution) of the chemical reaction. In order for the metal to be inert, it must have a relatively positive standard reduction potential. Common passive electrodes are constructed from Ag, Pt, and Au.

3. **Distinguish between a galvanic and an electrolytic cell. Which type of cell would be used to nickel plate a faucet? Which type of cell can act as a battery?**

A galvanic cell converts chemical potential energy into electrical potential energy, while an electrolytic cell converts electrical potential energy into chemical potential energy. Spontaneous electron transfer reactions give off free energy as they lower their chemical potential energy. The released energy is converted into electrical potential energy in a galvanic cell. Batteries are galvanic cells. Reactions in which the products are at a higher free energy than the reactants can be forced to the higher chemical potential energy by an external power supply in an electrolytic cell, which converts the electrical potential energy stored in the power supply into the higher chemical potential energy of the reactants. Nickel plating is done in an electrolytic cell.

5. **Sn/Sn²⁺ (1.0 M) and Zn/Zn²⁺ (1.0 M).**

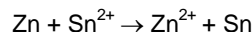
- a) **What is the anode half-reaction?** The one with the more negative standard reduction potential



- b) **What is the cathode half-reaction?** The one with the more positive standard reduction potential



- c) **What is the cell reaction?**

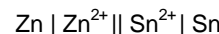


- d) **What are the oxidizing and reducing agents?**



- e) **How many electrons are transferred in the cell reaction?** 2 electrons

- f) **What is the abbreviated form of the cell?**

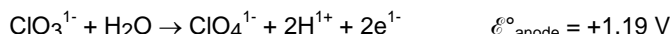


- g) **What is the cell potential?**

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = -0.14 - (-0.76) = 0.62 \text{ V}$$

7. **Au/Au³⁺ (1.0 M) and ClO₃¹⁻ (1.0 M)/ClO₄¹⁻ (1.0 M).**

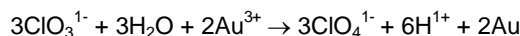
- a) **What is the anode half-reaction?** The one with the less positive standard reduction potential



- b) **What is the cathode half-reaction?** The one with the more positive standard reduction potential



- c) **What is the cell reaction?**



- d) **What are the oxidizing and reducing agents?**



- e) **How many electrons are transferred in the cell reaction?** 6 electrons

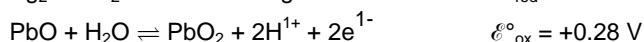
- f) **What is the abbreviated form of the cell?**



- g) **What is the cell potential?**

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = +1.50 - 1.19 = 0.31 \text{ V}$$

- e) **Ag₂O(s) + PbO(s) → 2Ag(s) + PbO₂(s)**

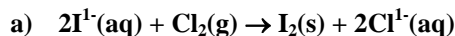


Note: $2\text{H}^{1+} + 2\text{OH}^{1-} = 2\text{H}_2\text{O}$ on right side cancels $2\text{H}_2\text{O}$ on left side.

$$\mathcal{E}^{\circ}_{\text{rxn}} = \mathcal{E}^{\circ}_{\text{red}} - \mathcal{E}^{\circ}_{\text{ox}} = 0.34 - 0.28 = 0.06 \text{ V} \quad \Delta G^{\circ} = -2 \text{ mol e}^{-} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^{-}} \times 0.06 \text{ V} = -1 \times 10^4 \text{ J} = -10 \text{ kJ}$$

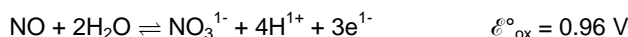
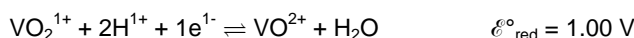
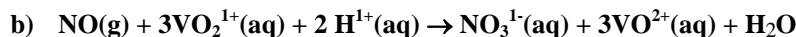
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9. Refer to Appendix E and determine ΔG° for the following reactions.



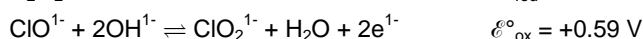
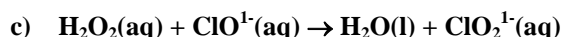
$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{red}} - \mathcal{E}^\circ_{\text{ox}} = 1.36 - 0.54 = 0.82 \text{ V}$$

Use Equation 9.4b to solve for ΔG° : $\Delta G^\circ = -2 \text{ mol e}^- \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times 0.82 \text{ V} = -1.6 \times 10^5 \text{ J} = -160 \text{ kJ}$



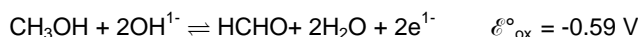
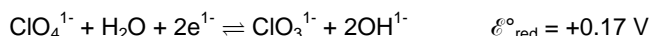
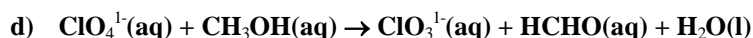
$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{red}} - \mathcal{E}^\circ_{\text{ox}} = 1.00 - 0.96 = 0.04 \text{ V}$$

Use Equation 9.4b to solve for ΔG° : $\Delta G^\circ = -3 \text{ mol e}^- \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times 0.04 \text{ V} = -1 \times 10^4 \text{ J} = -10 \text{ kJ}$



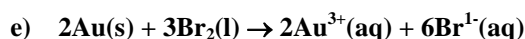
$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{red}} - \mathcal{E}^\circ_{\text{ox}} = 0.88 - 0.59 = 0.29 \text{ V}$$

$$\Delta G^\circ = -2 \text{ mol e}^- \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times 0.29 \text{ V} = -5.6 \times 10^4 \text{ J} = -56 \text{ kJ}$$



$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{red}} - \mathcal{E}^\circ_{\text{ox}} = 0.17 - (-0.59) = 0.76 \text{ V}$$

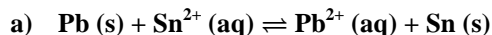
$$\Delta G^\circ = -2 \text{ mol e}^- \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times 0.76 \text{ V} = -1.5 \times 10^5 \text{ J} = -150 \text{ kJ}$$



$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{red}} - \mathcal{E}^\circ_{\text{ox}} = 1.09 - 1.50 = -0.41 \text{ V}$$

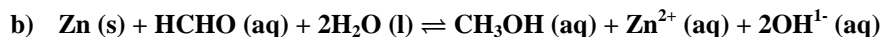
$$\Delta G^\circ = -6 \text{ mol e}^- \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol e}^-} \times (-0.41 \text{ V}) = +2.4 \times 10^5 \text{ J} = 240 \text{ kJ}$$

11. Determine the equilibrium constants for the following reactions.



$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = -0.14 - (-0.13) = -0.01 \text{ V}$$

Use Equation 9.7 to determine, K. $\log K = (16.9)(2)(-0.01) = -0.34$, so $K = 10^{-0.34} = 0.46$



$$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = -0.59 - (-0.76) = +0.17 \text{ V}$$

Use Equation 9.7 determine K. $\log K = (16.9)(2)(0.17) = 5.7$, so $K = 5 \times 10^5$

13. Given the following half-reactions,



Construct a cell with the following cell reaction: $\text{Ni}^{2+} + 6\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}$

a) What is the standard cell potential? $\mathcal{E}^{\circ}_{\text{cell}} = -0.23 - (-0.47\text{V}) = 0.24\text{V}$

b) What is the value of ΔG° for the reaction?

$$\Delta G^{\circ} = -n \mathcal{F} \mathcal{E}^{\circ} = -(2 \text{ mol e}^{-1}/\text{mol})(9.65 \times 10^4 \text{ C/mol e}^{-1})(0.24\text{V}) = -46 \text{ kJ/mol}$$

c) What is the equilibrium constant as determined from the cell potential?

The reaction is a two-electron transfer, so we use $n=2$ in Equation 9.7.

$$\log K = 16.9n \mathcal{E}^{\circ}_{\text{cell}} = (16.9)(2)(0.24) = 8.1, \text{ so } K = 10^{8.1} = 1.3 \times 10^8$$

d) What is this equilibrium constant called? The formation constant of $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

15. Write the cell reaction and the equilibrium constant expression for and determine the cell potentials at 25 °C of the following electrochemical cells:

Use $\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{red}} - \mathcal{E}^{\circ}_{\text{ox}}$ to obtain the standard cell potential and the Nernst equation (Eq. 9.5) for the cell potential.

a) $\text{Cr} \mid \text{Cr}^{3+} (0.06 \text{ M}) \parallel \text{Ag}^{1+} (0.68 \text{ M}) \mid \text{Ag}$



$$Q = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^{1+}]^3} = \frac{0.060}{0.68^3} = 0.191; \quad \mathcal{E}_{\text{cell}} = 1.54 - \frac{0.0592}{3} \log(0.191) = 1.55 \text{ V}$$

b) $\text{Pt} \mid \text{Sn}^{4+} (0.041 \text{ M}), \text{Sn}^{2+} (0.12 \text{ M}) \parallel \text{Cu}^{2+} (0.84 \text{ M}), \text{Cu}^{1+} (0.0084 \text{ M}) \mid \text{Ag}$

The $\text{Sn}^{2+}/\text{Sn}^{4+}$ couple is in the anode, so it must be the oxidation, while the $\text{Cu}^{1+}/\text{Cu}^{2+}$ couple in the cathode and is the reduction. Silver is a passive electrode in each compartment.



$$Q = \frac{[\text{Sn}^{4+}][\text{Cu}^{1+}]^2}{[\text{Sn}^{2+}][\text{Cu}^{2+}]^2} = \frac{(0.041)(0.0084)^2}{(0.12)(0.84)^2} = 3.42 \times 10^{-5}; \quad \mathcal{E}_{\text{cell}} = 0.01 - \frac{0.0592}{2} \log(3.42 \times 10^{-5}) = 0.14 \text{ V}$$

c) $\text{Ti} \mid \text{Ti}^{2+} (0.020 \text{ M}) \parallel \text{Au}^{3+} (1.0 \text{ M}) \mid \text{Au}$



$$Q = \frac{[\text{Ti}^{2+}]^3}{[\text{Au}^{3+}]^2} = \frac{(0.020)^3}{(1.0)^2} = 8.0 \times 10^{-9}; \quad \mathcal{E}_{\text{cell}} = 3.13 - \frac{0.0592}{6} \log(8.0 \times 10^{-9}) = 3.21 \text{ V}$$

17. Consider the cell: $\text{Pb}(\text{s}) \mid \text{Pb}^{2+}(\text{aq}) \parallel \text{Ag}^{1+}(\text{aq}) \mid \text{Ag}(\text{s})$. What effect would each of the following have on $\mathcal{E}^{\circ}_{\text{cell}}$?

a) enlarging the lead electrode

The cell potential will not change. Solids have an activity of one, so changing the amount of solid does not change the reaction quotient, Q .

b) dissolving KCl in the anode

Addition of KCl to the anode compartment would precipitate PbCl_2 , which would decrease the concentration of Pb^{2+} . Pb^{2+} is a product, so the effect is to decrease Q , which makes ΔG more negative and increases the cell potential.

c) dissolving KCl in the cathode

Addition of KCl to the cathode compartment precipitates AgCl and decreases the concentration of Ag^{1+} . Ag^{1+} is a reactant, so the effect is to increase Q , which makes ΔG more positive and decreases the cell potential.

d) adding water to the cathode

Addition of water to the cathode compartment would dilute the solution, reducing the concentration of Ag^{1+} . As described in part c) this would lead to a decrease in cell potential.

e) reducing the volume of the solution in the anode

By pouring some of the solution out of the anode compartment, thus reducing the volume, no change in concentration of reactants or products takes place. Therefore, as long as the anode (electrode) remains in contact with the solution, no change in cell potential will occur

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19. The following cell has a potential of 0.27 V at 25 °C: $\text{Pt(s)}|\text{H}_2(1\text{atm}), \text{H}^{1+}(\text{? M})||\text{Ni}^{2+}(1\text{ M})|\text{Ni(s)}$

What is the pH of the solution in the anode compartment?

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592}{n} \times \log [\text{H}_3\text{O}^{1+}]^2 = \mathcal{E}^\circ - \frac{0.0592}{n} \times 2 \times \log [\text{H}_3\text{O}^{1+}]$$

$$0.27 = -0.23 - \frac{0.0592}{2} \times 2 \times \log [\text{H}_3\text{O}^{1+}] = -0.23 - 0.0592 \times \log [\text{H}_3\text{O}^{1+}]$$

$-0.0592 \times \log [\text{H}_3\text{O}^{1+}] = -0.0592$ pH, so we can rewrite the above as

$$0.27 = -0.23 + 0.0592 \text{ pH} \rightarrow \text{pH} = 16.9(0.27 + 0.23) = 8.5$$

21. Calculate \mathcal{E}° , \mathcal{E} and ΔG for the reaction: $3\text{Cu}^{2+} + 2\text{Al(s)} \rightarrow 2\text{Al}^{3+} + 3\text{Cu(s)}$ when $[\text{Cu}^{2+}] = 0.010\text{ M}$ and $[\text{Al}^{3+}] = 0.0085\text{ M}$.

Use Appendix E to obtain standard reduction potentials.



$$\mathcal{E}^\circ_{\text{rxn}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 0.34 - (-1.66) = +2.00\text{ V}$$

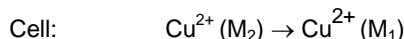
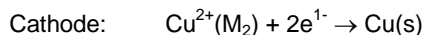
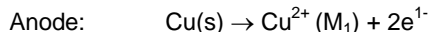
Write the Nernst Equation for this reaction (Eq. 9.5): $\mathcal{E}_{\text{rxn}} = \mathcal{E}^\circ_{\text{rxn}} - \frac{0.0592}{n} \log \left(\frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \right)$

$$\text{Solve the equation for } \mathcal{E}_{\text{rxn}}: \mathcal{E}_{\text{rxn}} = 2.00\text{ V} - \frac{0.0592}{6} \log \left(\frac{0.0085^2}{0.010^3} \right) = 1.98\text{ V}$$

$$\text{Solve Equation 9.4a: } \Delta G = -n\mathcal{F}\mathcal{E} = -\frac{6\text{ mol e}^{-1}}{1\text{ mol}} \times \frac{9.65 \times 10^4\text{ C}}{1\text{ mol e}^{-1}} \times 1.98\text{ V} = -1.15 \times 10^6\text{ J/mol} = -1.15 \times 10^3\text{ kJ/mol}$$

23. A concentration cell is an electrochemical cell in which the cell potential is developed from concentration differences only. Consider the following concentration cell: $\text{Cu}|\text{Cu}^{2+}(\text{M}_1)||\text{Cu}^{2+}(\text{M}_2)|\text{Cu}$, where M_1 and M_2 are the molar concentrations.

a) Write the two half-reactions and the net cell reaction.



b) Explain why $\mathcal{E}^\circ = 0$ for a concentration cell.

The two standard half-cell potentials are identical because the concentrations of the standard half-cells are identical ($\text{M}_1 = \text{M}_2 = 1.0\text{ M}$).

c) Write the expression for the Nernst equation for the cell at 25 °C.

$$\mathcal{E} = -\frac{0.0592}{2} \log \frac{\text{M}_1}{\text{M}_2} = +\frac{0.0592}{2} \log \frac{\text{M}_2}{\text{M}_1}$$

d) What must be true about the relative values of M_1 and M_2 if the cell is to function as a galvanic cell?

$\text{M}_2 > \text{M}_1$ (the concentration in the cathode must be greater than the concentration in the anode) for the process to be spontaneous.

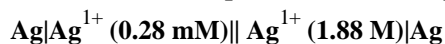
e) What would be the equilibrium concentration of Cu^{2+} in each half-cell?

$$[\text{Cu}^{2+}]_{\text{eq}} = \frac{1}{2} (\text{M}_1 + \text{M}_2) \text{ in each half cell.}$$

f) What happens to the mass of the electrode in the compartment on the left of the abbreviated cell?

The compartment on the left is the anode, so the copper electrode would dissolve, i.e., its mass would decrease.

25. Determine the cell potential and the equilibrium concentrations of the following concentration cell:



Use the result of Exercise 23c with the change that the reactions are one electron transfers

$$\mathcal{E} = +\frac{0.0592}{1} \log \frac{\text{M}_2}{\text{M}_1} = \frac{0.0592}{1} \log \frac{1.88}{2.8 \times 10^{-4}} = 0.23\text{ V}$$

$$[\text{Ag}^{1+}]_{\text{eq}} = \frac{1}{2} (0.00028 + 1.88) = 0.94\text{ M in each cell}$$

27. Assume that each of the solutions in the half-cells in Exercise 25 has a total volume of 150. mL and determine the mass change that the electrode in the cathode compartment must undergo to reach equilibrium.

The equilibrium concentration of each cell is 0.94 M, so the change in the anode is $1.88 - 0.94 = 0.94$ M. Therefore, $(0.150 \text{ L})(0.94 \text{ mol/L}) = 0.14 \text{ mol}$ of Ag^{1+} must deposit on the silver electrode. The mass change of the electrode is $(0.14 \text{ mol})(108 \text{ g/mol}) = 15.2 \text{ g}$.

29. One of the advantages of electrochemistry is that we have control of the free energy of the electrons. Explain how we have that control and how it can be used.

The free energy of the electrons can be controlled with a power supply, which extracts electrons from one electrode and injects electrons into the other. The fermi level and the free energy of the electrons in the electrode drops as electrons are withdrawn, and increases as electrons are injected. The free energy difference between the two electrodes can be used to drive reactions uphill in free energy.

31. How many moles of electrons are required to produce a charge of 1.0 coulomb?

$$1.0 \text{ C} \times \frac{1 \text{ mole electrons}}{96,485 \text{ C}} = 1.0 \times 10^{-5} \text{ mole electrons}$$

33. Consider the diagram of an electrolytic shown in the text.

- a) Toward which electrode, (+) or (-) do the magnesium ions migrate?

Mg^{2+} ions migrate toward the (-) electrode.

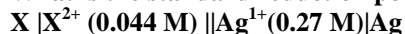
- b) What is the electrical sign of the anode? How does this compare to a galvanic cell?

The anode is positive, the opposite of a galvanic cell.

- c) In which direction do the electrons flow, anode \rightarrow cathode or cathode \rightarrow anode? How does this compare to a galvanic cell?

Electrons flow from anode \rightarrow cathode, the same as a galvanic cell.

35. What is the standard reduction potential of the X^{2+}/X couple if the cell potential of the following cell is 0.44 V?



The cell reaction is $\text{X} + 2\text{Ag}^{1+} \rightarrow \text{X}^{2+} + 2\text{Ag}$

Solve the Nernst equation for \mathcal{E}° :
$$\mathcal{E}^\circ = \mathcal{E} + \frac{0.0592}{n} \log \frac{[\text{X}^{2+}]}{[\text{Ag}^{1+}]^2} = 0.44 + \frac{0.0592}{2} \log \frac{0.044}{(0.27)^2} = 0.43 \text{ V}$$

$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 0.43 \text{ V}$, where $\mathcal{E}^\circ_{\text{anode}}$ is the standard reduction potential of the X^{2+}/X couple.

$\mathcal{E}^\circ_{\text{anode}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ = 0.80 - 0.43 = 0.37 \text{ V}$

37. Ignore overpotential effects and write the anode and cathode reactions occurring in the electrolysis of aqueous solutions of the following substances?

The species that is oxidized first is the best reducing agent (most negative reduction potential), and the species that is reduced first is the best oxidizing agent (most positive reduction potential). Furthermore, water is a possible reactant at either electrodes in the electrolysis of aqueous solutions. The electrolysis half-reactions are shown in bold.

| | <u>possible anode reactions</u> | <u>possible cathode reactions</u> | |
|-------------------------|--|---|---------------------------|
| FeSO₄ | $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^{1+} + 4\text{e}^{1-}$ $2\text{SO}_4^{2-} \rightleftharpoons \text{S}_2\text{O}_8^{2-} + 2\text{e}^{1-}$ | $+0.82 \text{ V } \text{Fe}^{2+} + 2\text{e}^{1-} \rightleftharpoons \text{Fe}$ $+2.01 \text{ V } 2\text{H}_2\text{O} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2 + 2\text{OH}^{1-}$ | -0.44 V -0.41 V |
| NiF₂ | $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^{1+} + 4\text{e}^{1-}$ $2\text{F}^{1-} \rightleftharpoons \text{F}_2 + 2\text{e}^{1-}$ | $+0.82 \text{ V } 2\text{H}_2\text{O} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2 + 2\text{OH}^{1-}$ $+2.87 \text{ V } \text{Ni}^{2+} + 2\text{e}^{1-} \rightleftharpoons \text{Ni}$ | -0.41 V -0.23 V |
| HI | $2\text{I}^{1-} \rightleftharpoons \text{I}_2 + 2\text{e}^{1-}$ $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^{1+} + 4\text{e}^{1-}$ | $+0.54 \text{ V } 2\text{H}_2\text{O} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2 + 2\text{OH}^{1-}$ $+0.82 \text{ V } 2\text{H}^{1+} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2$ | -0.41 V -0.00 V |
| AgNO₃ | $2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^{1+} + 4\text{e}^{1-}$ | $+0.82 \text{ V } 2\text{H}_2\text{O} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2 + 2\text{OH}^{1-}$ $\text{Ag}^{1+} + \text{e}^{1-} \rightleftharpoons \text{Ag}$ | -0.41 V +0.80 V |

Note that NO_3^{1-} is not an oxidizing agent in the absence of acid, H^{1+}

Electrochemistry

39. How many coulombs are required to reduce 3.0 moles of nitrate ion to ammonia?

The oxidation state of N is +5 in NO_3^{1-} and -3 in NH_3 . Thus, 8 mol e^{1-} are required for each mole of NO_3^{1-} .

$$3 \text{ mol NO}_3^{1-} \times \frac{8 \text{ mol } e^{1-}}{1 \text{ mol NO}_3^{1-}} \times \frac{96,500 \text{ C}}{1 \text{ mol } e^{1-}} = 2.3 \times 10^6 \text{ C}$$

41. A Nicad battery involves the following cell reaction: $\text{NiO}_2(\text{s}) + \text{Cd}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$ How many grams of NiO_2 are required in a Nicad battery rated at 1.0 A-hr? A rating of one A-hr means that the battery has enough reactant to support drawing 1 ampere of current for one hour.

$$3600\text{s} \times \frac{1 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^{1-}}{96,500 \text{ C}} \times \frac{\text{mol NiO}_2}{2 \text{ mol } e^{1-}} \times \frac{90.7 \text{ g}}{1 \text{ mol}} = 1.7 \text{ g}$$

43. Determine the concentration of Ni^{2+} in a solution if 90.5 C is required to reduce all of the Ni^{2+} in 25.0 mL of the solution.

$$90.5 \text{ C} \times \frac{1 \text{ mol } e^{1-}}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol Ni}^{2+}}{2 \text{ mol } e^{1-}} = 4.69 \times 10^{-4} \text{ mol Ni}^{2+} \quad \left[\text{Ni}^{2+} \right] = \frac{4.69 \times 10^{-4} \text{ mol Ni}^{2+}}{0.025 \text{ L}} = 1.88 \times 10^{-2} \text{ M}$$

45. Electrochemical machining is a process in which a metal can be removed (etched) selectively by making it the anode in an electrolytic cell. It is essentially the reverse of metal electroplating and can be thought of as externally enforced corrosion. Electrochemical machining is used in the aerospace and automobile industries for shaping metal parts, and electrochemical micromachining is seeing increased use in the microelectronics industry for creating intricate wiring patterns on microcircuit boards. Consider a 35 mm thick uniform copper foil layer of 5.0 cm x 5.0 cm square geometry on a circuit board.

a) Write the electrochemical half-reaction for this process and its standard reduction potential.



b) How many coulombs must be passed to remove 74 % of the volume of the copper foil. $d_{\text{Cu}} = 9.0 \text{ g/cm}^3$.

$$5.0 \text{ cm} \times 5.0 \text{ cm} \times (35 \times 10^{-4} \text{ cm}) \times \frac{9.0 \text{ g Cu}}{\text{cm}^3} \times \frac{1 \text{ mol Cu}}{63.546 \text{ g Cu}} \times \frac{2 \text{ mol } e^{1-}}{1 \text{ mol Cu}} \times \frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol } e^{1-}} \times 0.74 = 1.7 \times 10^3 \text{ C}$$

c) Approximately how many layers of copper atoms are there in a 35 μm thick foil. The radius of Cu is 1.3 \AA .

$$3.5 \times 10^{-5} \text{ m} \times \frac{1 \text{ layer}}{2.6 \times 10^{-10} \text{ m}} = 1.4 \times 10^5 \text{ layers}$$