GENERAL

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.

2. Use Equation 9.3 to define the volt.

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?

In Exercises 4 - 7, construct galvanic cells from the given couples and answer the following questions about each cell:

- **a)** What is the anode half-reaction?
- **b)** What is the cathode half-reaction?
- **c)** What is the cell reaction?
- **d)** What are the oxidizing and reducing agents?
- **e)** How many electrons are transferred in the cell reaction?
- **f)** What is the abbreviated form of the cell? Use a Pt wire as a passive electrode where needed.
- **g)** What is the cell potential?

4. Pb/Pb^{2+} (1.0 M) and Ag/Ag^{1+} (1.0 M) - See instructions above.

5. Sn/Sn^{2+} (1.0 M) and Zn/Zn^{2+} (1.0 M) - See instructions above.

6. Fe^{2+} (1.0 M)/Fe^{3+} (1.0 M) and Al/Al^{3+} (1.0 M) - See instructions above.

7. Au/Au^{3+} (1.0 M) and ClO_4^{1-} (1.0 M)/ClO_3^{1-} (1.0 M) - See instructions above.

THERMODYNAMICS AND ELECTROCHEMICAL CELLS

8. Refer to Appendix E and determine ΔG^o for the following reactions.

- **a)** $2Fe^{3+} + Pb(s) \rightarrow 2Fe^{2+} + Pb^{2+}$
- **b)** $H_2(g) + Cu^{2+} \rightarrow Cu(s) + 2H^{1+}$
- **c)** $Hg^{2+} + 2Ag(s) \rightarrow Hg(l) + 2Ag^{1+}$
- **d)** $2ClO_2^{1-} \rightarrow ClO^{1-} + ClO_3^{1-}$
- **e)** $Ag_2O(s) + PbO(s) \rightarrow 2Ag(s) + PbO_2(s)$

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

- **a)** $2I^{1-} + Cl_2(g) \rightarrow I_2(s) + 2Cl^{1-}$
- **b)** $2NO(g) + H_2O + 3VO_2^{1+} \rightarrow 2NO_3^{1-} + 3VO^{2+} + 2H^{1+}$
- **c)** $H_2O_2 + ClO^{1-} \rightarrow H_2O + ClO_2^{1-}$
- **d)** $ClO_4^{1-} + CH_3OH(aq) \rightarrow ClO_3^{1-} + HCHO + H_2O$
- **e)** $2Au(s) + 3Br_2(l) \rightarrow 2Au^{3+} + 6Br^{1-}$

10. Determine equilibrium constants for the following reactions.

- **a)** $BrO^{1-} + H_2O + 2Fe^{2+} \rightleftharpoons 2Fe^{3+} + Br^{1-} + 2OH^{1-}$
- **b)** $O_3(g) + 2Cl^{1-} + 2H^{1+} \rightleftharpoons O_2(g) + Cl_2(g) + H_2O$

11. Determine the equilibrium constants for the following reactions.

- **a)** $Pb(s) + Sn^{2+} \rightleftharpoons Pb^{2+} + Sn(s)$
- **b)** $Zn(s) + HCHO(aq) + 2H_2O \rightleftharpoons CH_3OH(aq) + Zn^{2+} + 2OH^{1-}$

12. Given the following half-reactions,

$AgCl(s) + e^{1-} \rightarrow Ag(s) + Cl^{1-}$ $\mathcal{E}^{\circ} = +0.22$ V

$Ag^{1+} + e^{1-} \rightarrow Ag(s)$ $\mathcal{E}^{\circ} = +0.80$ V

Construct a cell with the following cell reaction: $AgCl(s) \rightarrow Ag^{1+} + Cl^{1-}$

a) What is the standard cell potential?

b) What is the value of ΔG^{o} for the reaction?

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

d) What is this equilibrium constant called?

13. Given the following half-reactions,

$Ni(NH_3)_6^{2+} + 2e^{1-} \rightarrow Ni(s) + 6NH_3(aq)$ $\mathcal{E}^{\circ} = -0.47$ V

$Ni^{2+} + 2e^{1-} \rightarrow Ni(s)$ $\mathcal{E}^{\circ} = -0.23$ V

Construct a cell with the following cell reaction:

$Ni^{2+} + 6\ NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}$

a) What is the standard cell potential?

b) What is the value of ΔG^{o} for the reaction?

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

d) What is this equilibrium constant called?

14. Consider the following cell: $Pb(s) \mid Pb^{2+} \parallel Ag^{1+} \mid Ag(s)$

a) In which direction do the electrons flow, Pb → Ag or Ag → Pb?

b) What is the electrical sign of the anode?

c) In which direction do the anions flow through the liquid junction (bridge), anode → cathode or cathode → anode?

15. Write the cell reaction and the equilibrium constant expression for and determine the cell potentials at 25 ^{o}C of the following electrochemical cells.

a) $Cr \mid Cr^{3+}$ (0.060 M) $\parallel Ag^{1+}$ (0.68 M) $\mid$ Ag

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

c) $Ti \mid Ti^{2+}$ (0.0020 M) $\parallel Au^{3+}$(1.0 M) $\mid$ Au

16. Write the cell reaction and the equilibrium constant expression for and determine the cell potentials at 25 ^{o}C of the following electrochemical cells.

a) $Cr \mid Cr^{3+}$ (0.060 M) $\parallel Ag^{1+}$ (0.68 M) $\mid$ Ag

b) $Cu \mid Cu^{2+}$ (0.0073M) $\parallel Cr^{3+}$ (0.11M),$Cr_2O_7^{2-}$ (0.046M),H^{1+} (1.0M) $\mid$ Au

c) $Pt \mid H_2$(1.0 atm), H^{1+} (3.5 mM) $\parallel Hg^{2+}$(0.060 M) $\mid$ Hg

THE EFFECT OF CONCENTRATION ON CELL POTENTIAL

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

a) enlarging the lead electrode

b) dissolving KCl in the anode

c) dissolving KCl in the cathode

d) adding water to the cathode

e) reducing the volume of the solution in the anode

18. Consider the following reaction taking place in an electrochemical cell:
$2Cr^{2+} + HClO(aq) + H^{1+} \rightarrow 2Cr^{3+} + Cl^{1-} + H_2O$
Predict the effect of the following changes on the cell voltage.
a) increasing [HClO] in the cathode
b) increasing pH of the cell solution of the cathode
c) increasing size of the inert electrodes
d) adding KCl solution to the cathode

19. The following cell has a potential of 0.27 V at 25 °C:
$Pt(s)|H_2(1atm), H^{1+}(?\ M) \| Ni^{2+}(1\ M)|Ni(s)$
What is the pH of the solution in the anode compartment?

20. For the following reaction:
$NiO_2(s) + 4H^{1+} + 2Ag(s) \rightarrow Ni^{2+} + 2H_2O + 2Ag^{1+}$ $\qquad \mathcal{E}° = 2.48$ V
What is the pH of the solution if $\mathcal{E} = 2.10$ V and $[Ag^{1+}]=[Ni^{2+}]=0.015$ M?

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

22. Calculate ΔG for the reaction: $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$ when $[Cu^{2+}] = 0.010$ M and $[Zn^{2+}] = 0.080$ M.

23. Consider the following concentration cell: $Cu|Cu^{2+}\ (M_1) \| Cu^{2+}\ (M_2)|Cu$, where M_1 and M_2 are the molar concentrations.
a) Write the two half-reactions and the net cell reaction.
b) Explain why $\mathcal{E}^o = 0$ for a concentration cell.
c) Write the expression for the Nernst equation for the cell at 25 °C.
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?
e) What is the final concentration in the cell when equilibrium is reached?
f) What happens to the mass of the electrode in the compartment on the left of the abbreviated cell?

24. Determine the cell potential and the equilibrium concentrations of the following concentration cell:
$Cu|Cu^{2+}\ (0.020\ M) \| Cu^{2+}\ (2.0\ M)|Cu$

25. Determine the cell potential and the equilibrium concentrations of the following concentration cell:
$Ag|Ag^{1+}\ (0.28\ mM) \| Ag^{1+}\ (1.88\ M)|Ag$

26. Assume that each of the solutions in the half-cells in Exercise 24 has a volume of 100. mL and determine the mass change that the electrode in the anode must undergo to reach equilibrium.

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

THE ELECTROLYTIC CELL

28. What is a Fermi level? What happens to the Fermi level of an electrode when electrons are withdrawn from it by a power supply?

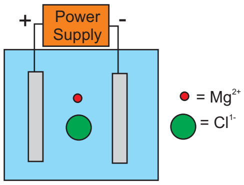
29. One of the advantages of electrochemistry is that we have control of the free energy of the electrons. Explain how we have that control and how it can be used.

30. What is a faraday?

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

32. What is overpotential? How is it important in the electrolysis of aqueous solutions?

33. Consider the diagram of an electrolytic cell shown below.



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

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

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

34. Consider the following cell:

$Cr | Cr^{3+}(1.00\ M) || Ni^{2+}(1.00\ M) | Ni \quad \mathcal{E}° = 0.68\ V.$

a) How many milligrams of metallic nickel would be plated on the cathode if a current of 0.11 A is drawn for 1.5 hrs?

b) What is the Cr^{3+} concentration when the Ni^{2+} concentration has dropped to 10^{-4} M? What is the cell potential at this point?

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

$X | X^{2+}\ (0.044\ M) || Ag^{1+}(0.27\ M) | Ag$

36. What is the standard reduction potential of Y^{3+} given that the cell potential of the following cell is 1.32 V?

$Zn | Zn^{2+}\ (0.14\ M) || Y^{3+}(1.2\ M) | Y$

PREDICTING THE PRODUCTS OF ELECTROLYSIS

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

a) $FeSO_4$ **b)** NiF_2 **c)** HI **d)** $AgNO_3$

38. Ignore overpotential effects and predict the products formed at the electrodes in the electrolysis of the following:

a) HF(aq) **b)** $BaCl_2$(l) **c)** KI(aq) **d)** KOH(aq)

QUANTITATIVE ASPECTS OF ELECTROCHEMISTRY

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

40. How long would a solution of $Cr_2(SO_4)_3$ have to be electrolyzed with a current of 3.0 A in order to deposit 10. g of Cr?

41. A Nicad battery involves the following cell reaction:

$NiO_2(s) + Cd(s) + 2\ H_2O \rightarrow Ni(OH)_2(s) + Cd(OH)_2(s)$

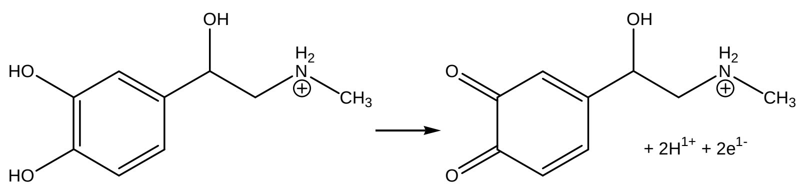
How many grams of NiO_2 are required in a Nicad battery rated at 1.0 A-hr? A rating of one A-hr means that the battery has enough reactant to support drawing 1 ampere of current for one hour.

42. A current of 0.600 A deposits 1.33 g of a certain metal in 1.00 hour. Assume a two-electron reduction to determine the atomic mass and identity of the metal.

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.

MISCELLANEOUS

44. Epinephrine (epp-uh-nef′-frin) is one of an important class of organic molecules known as catecholamines (cat-uh-cole′-amines), which function in living organisms as chemical messengers. Epinephrine is stored inside biological cells in extremely tiny sacs known as vesicles until they are secreted when a chemical signal is received, causing rupture of the vesicle and release of the contents, a process known as exocytosis. Electrochemical detection of epinephrine released from vesicles can be performed using inert microscopic carbon electrodes, which oxidize epinephrine according to the reaction below



a) If 1.1×10^{-12} C of charge resulted from the oxidation of all the epinephrine released from a spherical vesicle of 300. nm diameter, how many epinephrine molecules were in the vesicle?

b) Calculate the molarity of epinephrine in the vesicle prior to its release. The volume of a sphere is $^4/_3\,\pi r^3$, 1 nm = 10^{-9} m, and 1 L = 1 dm^3.

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 *micro*machining is seeing increased use in the microelectronics industry for creating intricate wiring patterns on microcircuit boards. Consider a 35 μm 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 of charge should be passed to remove 74 % of the volume of the copper foil? The density of copper is 9.0 $g\cdot cm^{-3}$.

c) How many layers of copper atoms are there in a 35 μm thick foil? The radius of a copper atom is 1.3 Å.

46. The world's aluminum is electrolytically extracted from the mineral bauxite, which is predominately hydrated aluminum oxide. This is a high-temperature process (1030 °C) in which bauxite is first converted into molten cryolite (Na_3AlF_6), which is then electrolytically reduced to molten aluminum metal. Although the mechanism is very complicated, the overall reaction is:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

Whereas the calculated thermodynamic cell potential for this reaction is -1.2 V, the actual cell potential in an industrial cell is -4.3 V.

a) Calculate the energy required, in $kJ\cdot mol^{-1}$, to industrially produce one ton of aluminum.

b) What fraction of this energy is wasted in the process?

c) Suggest a possible reason for the large disparity between the thermodynamic cell potential and the actual cell potential.