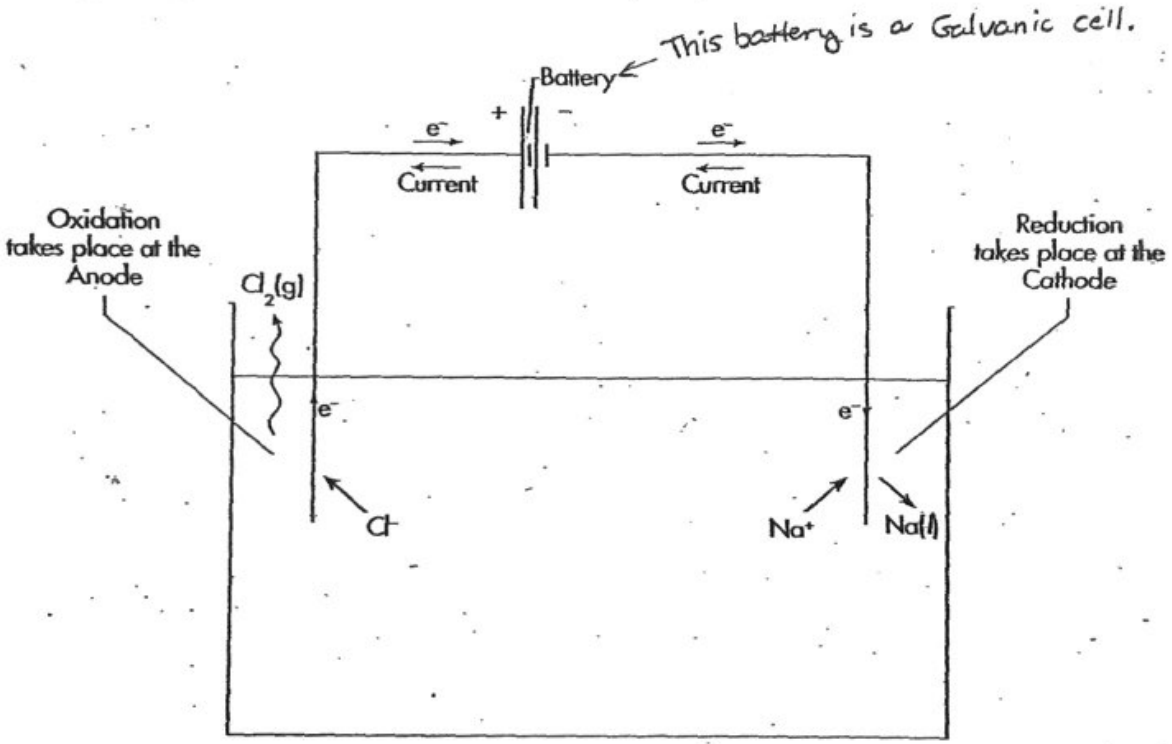
ELECTROLYTIC CELLS

In an electrolytic cell, an outside source of voltage is used to force a nonspontaneous redox reaction to take place. Let's look at the electrolysis of molten NaCl.

$2\ Na^+(molten) + 2\ Cl^-(molten) \rightarrow 2\ Na(l) + Cl_2(g)$		$E° = -4.07$ V
Oxidation:	$2\ Cl^-(molten) \rightarrow Cl_2(g) + 2\ e^-$	$E° = -1.36$ V
Reduction:	$2\ Na^+(molten) + 2\ e^- \rightarrow 2\ Na(l)$	$E° = -2.71$ V

An electrolytic cell that forces this reaction to take place is shown below.



In this process, pure liquid sodium and pure chlorine gas are generated from molten sodium chloride. Notice that the process does not take place in aqueous solution. That's because water is more easily reduced than Na^+, so water would be reduced instead of sodium ions in an aqueous solution.

The AN OX/RED CAT rule applies to the electrolytic cell in the same way that it applies to the galvanic cell.

Electrolytic cells are used for electroplating. You might see a question on the test that gives you an electrical current and asks you how much metal "plates out."

There are roughly four steps for figuring out electrolysis problems.

1. **If you know the current and the time, you can calculate the charge in coulombs.**

$$I = \frac{q}{t}$$

I = current (amperes, A)
q = charge (coulombs, C)
t = time (sec)

Amperes = Coulombs / Second

2. Once you know the charge in coulombs, you know how many electrons were involved in the reaction.

$$\text{Moles of electrons} = \frac{\text{coulombs}}{96{,}500 \text{ coulombs / mol}}$$

3. When you know the number of moles of electrons and you know the half-reaction for the metal, you can find out how many moles of metal plated out. For example: From this half-reaction for gold:

$$Au^{3+} + 3\,e^- \rightarrow Au(s)$$

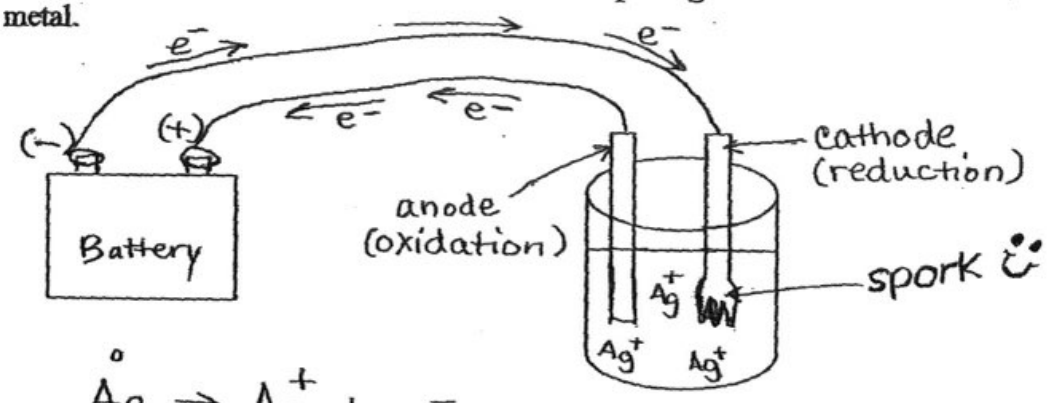
you know that for every 3 moles of electrons consumed, you get 1 mole of gold.

4. Once you know the number of moles of metal, you can use what you know from stoichiometry to calculate the number of grams of metal.

A galvanic cell produces current when an oxidation-reduction reaction proceeds spontaneously. A similar apparatus, an electrolytic cell, uses electrical energy to produce a chemical change. The process of **electrolysis** involves forcing a current through a cell to produce a chemical change for which the cell potential is negative; that is electrical work causes an otherwise nonspontaneous chemical reaction to occur. Electrolysis has great practical importance – charging a battery, producing aluminum metal, and chrome plating an object are all done by electrolysis.

Electroplating

The electrolyte solution must contain ions of the plating metal.



$$Ag \rightarrow Ag^+ + e^-$$

$$Ag^+ + e^- \rightarrow Ag$$

The overall reaction and equilibrium constant value are

$$2Cr^{2+}(aq) + Co^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + Co(s) \quad K = 2.79 \times 10^{7}$$

Calculate the cell potential, $\mathscr{E}$, for this galvanic cell and ΔG for the cell reaction at these conditions.

73. Calculate K_{sp} for iron(II) sulfide given the following data:

$$FeS(s) + 2e^- \rightarrow Fe(s) + S^{2-}(aq) \qquad \mathscr{E}^\circ = -1.01\ V$$
$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad \mathscr{E}^\circ = -0.44\ V$$

74. For the following half-reaction, $\mathscr{E}^\circ = -2.07$ V:

$$AlF_6^{3-} + 3e^- \longrightarrow Al + 6F^-$$

Using data from Table 17.1, calculate the equilibrium constant at 25°C for the reaction

$$Al^{3+}(aq) + 6F^-(aq) \rightleftharpoons AlF_6^{3-}(aq) \quad K = ?$$

75. Calculate the value of the equilibrium constant for the reaction of zinc metal in a solution of silver nitrate at 25°C.

76. The solubility product for CuI(s) is 1.1×10^{-12}. Calculate the value of $\mathscr{E}^\circ$ for the half-reaction

$$CuI + e^- \longrightarrow Cu + I^-$$

Electrolysis

77. How long will it take to plate out each of the following with a current of 100.0 A?
   a. 1.0 kg Al from aqueous Al^{3+}
   b. 1.0 g Ni from aqueous Ni^{2+}
   c. 5.0 mol Ag from aqueous Ag^+

78. The electrolysis of BiO^+ produces pure bismuth. How long would it take to produce 10.0 g of Bi by the electrolysis of a BiO^+ solution using a current of 25.0 A?

79. What mass of each of the following substances can be produced in 1.0 h with a current of 15 A?
   a. Co from aqueous Co^{2+}
   b. Hf from aqueous Hf^{4+}
   c. I_2 from aqueous KI
   d. Cr from molten CrO_3

80. Aluminum is produced commercially by the electrolysis of Al_2O_3 in the presence of a molten salt. If a plant has a continuous capacity of 1.00 million amp, what mass of aluminum can be produced in 2.00 h?

81. An unknown metal M is electrolyzed. It took 74.1 s for a current of 2.00 amp to plate out 0.107 g of the metal from a solution containing $M(NO_3)_3$. Identify the metal.

82. Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 s deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

83. What volume of F_2 gas, at 25°C and 1.00 atm, is produced when molten KF is electrolyzed by a current of 10.0 A for 2.00 h? What mass of potassium metal is produced? At which electrode does each reaction occur?

84. What volumes of $H_2(g)$ and $O_2(g)$ at STP are produced from the electrolysis of water by a current of 2.50 A in 15.0 min?

85. One of the few industrial-scale processes that produce organic compounds electrochemically is used by the Monsanto Company to produce 1,4-dicyanobutane. The reduction reaction is

$$2CH_2{=}CHCN + 2H^+ + 2e^- \longrightarrow NC{-}(CH_2)_4{-}CN$$

The $NC{-}(CH_2)_4{-}CN$ is then chemically reduced using hydrogen gas to $H_2N{-}(CH_2)_6{-}NH_2$, which is used in the production of nylon. What current must be used to produce 150 g of $NC{-}(CH_2)_4{-}CN$ per hour?

86. A single Hall–Heroult cell (as shown in Fig. 17.22) produces about 1 ton of aluminum in 24 hours. What current must be used to accomplish this?

87. It took 2.30 min using a current of 2.00 A to plate out all the silver from 0.250 L of a solution containing Ag^+. What was the original concentration of Ag^+ in the solution?

88. A solution containing Pt^{4+} is electrolyzed with a current of 4.00 A. How long will it take to plate out 99% of the platinum in 0.50 L of a 0.010 *M* solution of Pt^{4+}?

89. A solution at 25°C contains 1.0 *M* Cd^{2+}, 1.0 *M* Ag^+, 1.0 *M* Au^{3+} and 1.0 *M* Ni^{2+} in the cathode compartment of an electrolytic cell. Predict the order in which the metals will plate out as the voltage is gradually increased.

90. Consider the following half-reactions:

$$IrCl_6^{3-} + 3e^- \longrightarrow Ir + 6Cl^- \qquad \mathscr{E}^\circ = 0.77\ V$$
$$PtCl_4^{2-} + 2e^- \longrightarrow Pt + 4Cl^- \qquad \mathscr{E}^\circ = 0.73\ V$$
$$PdCl_4^{2-} + 2e^- \longrightarrow Pd + 4Cl^- \qquad \mathscr{E}^\circ = 0.62\ V$$

A hydrochloric acid solution contains platinum, palladium, and iridium as chloro-complex ions. The solution is a constant 1.0 *M* in chloride ion and 0.020 *M* in each complex ion. Is it feasible to separate the three metals from this solution by electrolysis? (Assume that 99% of a metal must be plated out before another metal begins to plate out.)

91. What reactions take place at the cathode and the anode when each of the following is electrolyzed?
   a. molten $NiBr_2$ b. molten AlF_3 c. molten MnI

92. What reactions take place at the cathode and the anode when each of the following is electrolyzed? (Assume standard conditions.)
   a. 1.0 *M* $NiBr_2$ solution
   b. 1.0 *M* AlF_3 solution
   c. 1.0 *M* MnI_2 solution

Additional Exercises

93. The saturated calomel electrode, abbreviated SCE, is used as a reference electrode in making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (Hg_2Cl_2). The electrolyte is saturated KCl. $\mathscr{E}_{SCE}$ is +0.242 V relative to the standard hydrogen electrode. Calculate the potential for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components at standard conditions. In each case indicate whether the SCE is the cathode or the anode. Standard reduction potentials are found in Table 17.1.