CHAPTER 7 LECTURE NOTES

7.1. Faraday's Laws of Electrolysis

- Mass of an element produced at an electrode is proportional to the amount of electrical charge Q passed through the liquid. If a current of I Amperes (A) is passed through an electrolyte solution for t seconds (s), we have

$$Q = It,$$

where the units of Q is the Coulomb (C). Obviously, C = A × s.

- The mass of element produced is proportional to the equivalent weight of the element.

The concept of "equivalent weights" is no longer recommended by IUPAC. However, it remains a useful concept in this context. One way to think about equivalent weight in the context of electrolysis is as the ratio of the molar mass (M) of the substance to the number of moles of electrons n that need to be added or removed to neutralize it. That is,

$$E = M/n.$$

To illustrate, the equivalent weights E of a few elements are:

Reaction	M (g mol^{-1})	n	E (g equiv^{-1})
$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	1.008	1	1.008
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	55.847	2	27.924
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	55.847	3	18.616
$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$	35.453	1	35.453

The two laws can be combined into a convenient form by introducing the quantity known as the Faraday (F), which is the charge carried by one mole of electrons:

$$F = 1.6022 \times 10^{-19}\ \text{C} \times 6.0220 \times 10^{23}\ \text{mol}^{-1}$$

$$= 96{,}485\ \text{C mol}^{-1}.$$

Since one mole of electrons corresponds to one equivalent of the element, we may also think of the units of the F as C equiv^{-1}.

The "Electrolysis" Equation:

Let us now combine the two laws of Faraday into one convenient equation that can be used in electrolysis problems.

To produce *w* grams or (*w*/*E*) equivalents of an element by electrolysis, we need (*w*/*E*) × *F* Coulombs of charge to pass through the solution. Mathematically,

$$Q = It = (w/E)F.$$

Now, using the definition $E = M/n$ in terms of molar mass, M, and number of moles of electrons, n, we write

$$\boxed{\begin{gathered}\frac{w}{(M/n)}F = It \text{ or} \\ \frac{wnF}{M} = It.\end{gathered}}$$

This equation or its various re-arranged forms can be used to solve all electrolysis problems.

Example 7.1, Problems 7.1 – 7.3

Example 7.1

a) To deposit 1.200 g of Au from Au^{3+} ($n = 3$), we need

$$\frac{1.2 \text{ g Au} \times 3 \text{ mol e}^-/\text{mol Au} \times 96485 \text{ C mol e}^{-1}}{196.97 \text{ g Au/mol Au}} = 1763.4 \text{ C}.$$

b) Time taken, using $I = 0.025$ A:

We rearrange the equation above to get

$$t = \frac{wnF}{MI}.$$

Substituting, we get

$$t = \frac{1763.4 \text{ C}}{0.025 \text{ C s}^{-1}} = 70536 \text{ s}.$$

c) From the equation given, for the liberation of O_2, $n = 4$. Therefore, we write

$$\frac{w}{M} = \frac{It}{nF} = \frac{0.025 \times 70536}{4 \times 96485} = 0.04569 \text{ mol}.$$

Assuming ideal behavior, this occupies 0.1132 L at 25°C and 1 bar.

Molar Conductivity and Arrhenius Theory

For electrolytes, the measured conductance (units: Ω^{-1} for Ohms^{-1} or S, for Siemens) is related to the surface area of the electrodes used, *A*, and the separation between them, *l*, as

$$G = \kappa(A/l),$$

where κ is a proportionality constant for each electrolyte, called *specific conductance* or **conductivity**. Obviously, κ must have units of S m^{-1} or S cm^{-1}). The ratio *A*/*l* is characteristic of the conductance cell used for measrement and is called the **cell constant**. **Molar conductivity**, Λ, is defined as

$$\Lambda = \kappa/c,$$

where *c* is the concentration. Concentration units must be carefully chosen so that there is no unit incompatibility between the numerator and the denominator.

See Example 7.2.

Arrhenius theory of weak electrolytes proposes that in weak electrolytes, there is a dynamical equilibrium between the undissociated electrolyte and the ions that result from the dissociation:

$$\mathrm{AB} \rightleftharpoons \mathrm{A}^{+} + \mathrm{B}^{-}.$$

The equilibrium constant in terms of concentration, K_C, can be written as

$$K_C = \frac{(n_{A^+}/V)(n_{B^-}/V)}{n \quad /V} = \frac{n_{A^+}n_{B^-}}{n \quad V}.$$

Because of the inverse-dependence on the volume, as the solution is diluted, the number of moles of the ions should increase. Arrhenius proposed that the an infinitely dilute solution of a weak electrolyte is completely dissociated. The molar conductivity, therefore, reaches a maximum, $\Lambda°$, and that this can be obtained by adding up the ionic molar conductivities:

$$\Lambda^\circ = \Lambda_{A^+} + \Lambda_{B^-}.$$

Since the conductance of a solution is proportional to the concentration of the ions present, Arrhenius proposed that the degree of dissociation α of any solution can be obtained as

$$\alpha = \frac{\Lambda}{\Lambda^\circ}.$$

Also, by using the definition of α , we obtain $\boxed{K_C = \frac{\alpha^2 c}{(1-\alpha)} = \frac{c(\Lambda/\Lambda^\circ)^2}{1-(\Lambda/\Lambda^\circ)}.}$

Problems 7.5–7.9, 7.12, 7.13.