Electrochemistry Unit Activity – Extracting Work from Chemical Change   KEY

The purpose of the electrochemical cell is to extract electrical work from chemical change or to use electrical work to force a non-spontaneous chemical change to occur. Consider the definition that work is equal to force times distance: ***w = Fd***. Earlier in this class we considered expansion work, ***w= -PΔV***, sometimes referred to as PV work. Now, we will consider electrical work, which is defined as charge times voltage: ***w=-QV***. (the negative signs is to keep track that work is done by the system). To relate electrical work to chemical change there is a fortunate situation that the change in the Gibbs free energy is equal to the maximum non-expansion work. The non-PV work is electrical work. Therefore, for a change in an electrochemical cell, **ΔG$_{rxn}$ = -(charge X voltage)**. The voltage is E, the potential of the cell. The total charge is the number of electrons per mole reaction, n, times Faraday's constant F. This gives the important relationship

$$\Delta G = -nFE$$

The bottom line is we now have a relationship between the ΔG$_{rxn}$ and the electric potential, E. Under standard conditions,

$$\Delta G^0 = -nFE^0$$

E° can therefore be related to the equilibrium constant K, since ΔG$_r$° = -RTlnK.

You will need the data to answer the following questions:

Standard reduction potential data:		Thermodynamic Data, Δ$_f$G° (kJ mol^{-1})	
$Al^{3+} + 3e^- \rightarrow Al$	E° = -1.66 V	Cu(s)	0
$Cu^{2+} + 2e^- \rightarrow Cu$	E°= +.34 V	Cu^{2+}(aq)	+65.5
		Al(s)	0
		Al^{3+}(aq)	-481.2

Let's think about the exciting demonstration in which we "dissolved" Al metal in a concentrated solution of $CuCl_2$(aq).

1. Write down the balanced REDOX reaction describing that demonstration.
   Use the method of half-reactions for accurate balancing. Aluminum was "dissolved" meaning it started out as a solid and became an ion floating in solution. In other words, it was oxidized.

   Oxidation ½ Reaction: 2Al (s) → 2Al³⁺ (aq)+ 6e⁻
   Reduction ½ Reaction: 3Cu²⁺ (aq) + 6e⁻→ 3Cu (s)

   Overall balanced: 2Al (s) + 3Cu²⁺ (aq) → 2Al³⁺ (aq) + 3Cu (s)

2. Using the given thermodynamic data, calculate the $\Delta G_{rxn}°$ for your balanced reaction.
   $\Delta G_{rxn}° = \Delta G_{products}° - \Delta G_{reactants}° = [3(0) + 2(-481.2)] – [2(0) + 3(65.5)] = -1158.9$ kJ/mol

3. Based on your value of $\Delta G_{rxn}°$ would you expect this reaction to be spontaneous?
   Yes, a negative ΔG indicates a spontaneous reaction.

4. Based on the computed value of the free energy, can you calculate the value of the equilibrium constant under standard conditions? If so, what is the value of K?
   Yes, we could.
   $\Delta G_{rxn}° = -RTln(K_{eq})$
   -1158900 J/mol $= -(8.314$ J/molK$)(298K)ln(K_{eq})$
   $ln(K_{eq}) = 467.76$
   $K_{eq} = e^{(467.76)} = \infty$ (essentially infinitely large!!!)

Now imagine running the same reaction in an electrochemical cell.

5. How might you construct a voltaic cell from these materials? What would serve as the anode? What would serve as the cathode? What ½ reaction would occur at the anode? At the cathode?
   A voltaic cell would have a positive cell potential. We know from the previous work in this activity, a positive cell potential can be achieved when aluminum is oxidized and copper is reduced.
   We would need a solid piece of aluminum to serve as the anode (oxidation site) and a solid piece of copper to serve as the cathode (reduction site).

   At the anode: Oxidation ½ Reaction: Al → Al^{3+} + 3e-
   At the cathode: Reduction ½ Reaction: Cu^{2+} + 2e- → Cu

6. What is the standard cell potential for your cell?
   We can calculate the standard cell potential $E° = E°_{cathode} – E°_{anode} = 0.34 – (-1.66) = 2V$

7. Calculate the amount of electrical work that can be extracted by running one mole reaction of this cell under standard conditions.
   $\Delta G_{rxn}° = -nFE°$ = -(6 mol e-)(96,485 C/mol e-)(0.34V – (-1.66V))
                = -(6 mol e-)(96,485 C/mol e-)(2V)
                = -1157820 J/mol   or   -1157.82 KJ/mol

8. Compare the amount of non expansion work done by this cell with the change in free energy you calculated in question 2.
   -1157.82 KJ/mol is pretty close to -1158.9 KJ/mol

9. Given that you have chosen standard conditions for your voltaic cell, what must the concentrations of the ions be?

Standard conditions are defined as the concentrations of any ions being 1M.

10. With these concentrations, is the system at equilibrium? If not, can you predict the direction of this reaction based on the standard concentrations? (hint: think Q vs K)
To decide whether or not the system is at equilibrium, we must compare Q to K.

Reaction: 2Al + 3Cu²⁺ → 2Al³⁺ + 3Cu

$$Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = \frac{[1M]^2}{[1M]^3} = 1$$

1 is much smaller than an essentially infinite K value. Thus, because Q is too small, more products must be made to reach equilibrium and the reaction will move forward (to the right).

11. When the system is at equilibrium, what will the value of E be?
At equilibrium, the cell potential is ZERO. Once equilibrium is reached, there is no driving force (EMF) pushing electrons. (a dead battery)

How might we determine the value of the cell potential under nonstandard conditions?
MINI LECTURE DERIVATION OF NERNST EQUATION

12. Determine the cell potential of the following cells:

<Al(s) | Al³⁺(.001M) || Cu²⁺(.01M) | Cu(s)>

<Al(s) | Al³⁺(1M) || Cu²⁺(10⁻⁸ M) | Cu(s)>

Remember here: $Q = \dfrac{[Al^{3+}]^2}{[Cu^{2+}]^3}$

First cell:
$$E = E^\circ - \left(\frac{0.0591}{n}\right)\log Q$$
$$E = 2V - \left(\frac{0.0591}{6}\right)\log\left(\frac{(0.001)^2}{(0.01)^3}\right) = 2V$$

Second Cell:
$$E = E^\circ - \left(\frac{0.0591}{n}\right)\log Q$$

$$E = 2V - \left(\frac{0.0591}{6}\right)\log\left(\frac{(1)^2}{(2 \times 10^{-8})^3}\right) = 1.76V$$