Lecture 14: $E^\circ_{\text{cell}}$ and $\Delta G$

• Reading: Zumdahl: 10.12 and 11.3

• Outline: The voltage of a battery is determined by the Gibbs free energy of the chemical reaction that happens inside the battery.
  – $E^\circ_{\text{cell}}$ and work
  – $E^\circ_{\text{cell}}$ and $\Delta G$
$E^\circ_{\text{cell}}$

- This is the symbol we will use to represent the voltage of a battery or EMF cell (in Volts).
- The naught (superscript) means under standard thermodynamic conditions.
- We saw in Lecture 13 how to construct a galvanic electrochemical cell (i.e. battery) that was capable of generating a flow of electrons.

- This flow of electrons (current) can be used to perform work on the surroundings.
**$E_{cell}$ and work**

- From the definition of electromotive force (emf):
  
  Volt = energy (J)/charge (C)
  
  1 Volt = 1 Joule/Coulomb

In English: 1 J of energy is available when 1 C of charge is transferred (or moves between) a potential difference of 1 V. (Think of gravity)

If all of this energy is converted to work that would be the maximum electrical work available due to the potential.

$Q$ is the symbol for the amount of charge in Coulombs

\[
E_{cell} = \frac{-\Delta E}{\Delta Q}
\]

\[
-\Delta E = E_{cell} \cdot \Delta Q = -w_{\text{max}}^{\text{elect}}
\]

Convention: If the battery potential is positive the system (battery) does work so (inside) it looses energy, hence the minus sign.
E°_{cell} example

How much work is done by a galvanic cell in which 1.5 moles of electrons are passed between a potential of 2 V, under standard thermodynamic conditions?

\[ E^o_{cell} \cdot \Delta Q = -w_{max}^{elect} \]

\[ 2V \cdot 1.5\text{moles} = ?? \]

\[ \uparrow \]

What do we do with this?
We need to know how much charge this is
The Faraday

How much charge does a mole of electrons have? The “Faraday” (F) is the amount of charge contained in 1 mole of electrons.

\[ F = 96,485 \, C/mol \sim 10^5 \, C/mol = 10^5 \, (J/mol)/V \]

\[ e = 1.6 \times 10^{-19} \, C \] (Charge on a single electron)

\[ F = N_A e \]

Now we can finish our problem and compute the work:

\[ \Delta Q = n \cdot F = 1.5 \text{ moles} \cdot (0.96548) \times 10^5 \, C/mol \]

\[ w_{\text{max}}^{\text{elect}} = -E_{\text{cell}} \cdot \Delta Q \]

\[ 
\approx -2V \cdot 1.5 \times 10^5 \, C = -3 \times 10^5 \, J = -300 \, kJ \\
= -290 \, kJ \text{(more sigfigs)}
\]

A 1V battery can give about 100 kJ of work per mole of “reactant”.
Free energy and Work

Section 10.12: The Gibbs Free energy is equal to the reversible useful (i.e. non PdV) work, at constant T and P

\[ \Delta G = w_{rev}^{\text{extra (non-pdv)}} = w_{\text{max}}^{\text{useful}} \]

Proof

\[ \Delta G = \Delta H - T \Delta S = \Delta E + P \Delta V - T \Delta S \]

Follow a reversible path:

\[ = q_{rev} + w_{rev} + P \Delta V - q_{rev} = w_{rev} + P \Delta V \]

\[ = -P \Delta V + w_{rev}^{\text{extra}} + P \Delta V = w_{rev}^{\text{extra}} \]
$E_{\text{cell}}$ and $\Delta G$

- Since there is a relationship between $\Delta G$ and work, there is also a relationship between $\Delta G$ and $E_{\text{cell}}$.

\[ \Delta G = \omega_{\text{max}}^{\text{elect}} = -E_{\text{cell}} \cdot \Delta Q \]

- The above relationship states that there is a direct relationship between Gibbs free energy and cell potential.

- For a galvanic cell (@ standard conditions):

\[ E^\circ_{\text{cell}} > 0 \quad \text{Therefore, } \Delta G^\circ < 0 \text{ (spontaneous)} \]
E_{cell} and ΔG_{rxn}

• We have a chemical reaction, and some of the reaction occurs (moles of each species are used up or created):

\[ \Delta n(i) = c_{ss,i} \Delta X \quad \text{and} \quad \Delta G = \Delta G_{rxn} \Delta X \]

• Some electrons are transferred in the reaction.

\[ \Delta n(e) = n(e) \Delta X \quad \text{and} \quad \Delta Q = F \Delta n(e) \]

• \( n(e) \) is the stoichiometric coefficient for the number of electrons transferred for the reaction as written (even though the electrons are not written out in the net reaction)

• Putting all these connections together in the equation on the previous slide:
Reaction Energy

- The relation between the actual energy and the reaction energy in terms of the balanced equations gives a relation between the **reaction** free energy and the cell voltage:
  \[
  \Delta G = -E_{cell} \cdot \Delta Q = -E_{cell} \cdot F \Delta n(e) = -E_{cell} \cdot Fn\Delta X
  \]
  \[
  \Delta G = \Delta G_{rxn} \Delta X = -E_{cell} \cdot Fn\Delta X
  \]
  \[
  \Delta G_{rxn} = -E_{cell} \cdot Fn
  \]

- To underscore what is written here, notice that the reaction Gibbs free energy is not the electrical work. Read your text very carefully because you cannot equate reaction energy and work. To do work you actually have to have some amount of chemical reaction (specified as the number of moles of something that reacted).

- Identify the intensive and extensive quantities above.
Determine $E^\circ_{\text{cell}}$ and $\Delta G^0_{\text{rxn}}$ for a Battery

For the following reaction, determine the overall standard cell potential and determine $\Delta G^0$

Note: The net reaction does not give n, and does not show how many electrons are used per reaction. To determine n(e) we must break the reaction into its half reactions.

\[
\text{Cd}^{+2}(aq) + \text{Cu}(s) \rightarrow \text{Cd}(s) + \text{Cu}^{+2}(aq)
\]

\[
\begin{align*}
\text{Cd}^{+2} + 2e^- & \rightarrow \text{Cd} & E^\circ_{1/2} = -0.40 \text{ V} \\
\text{Cu}^{+2} + 2e^- & \rightarrow \text{Cu} & E^\circ_{1/2} = +0.34 \text{ V} \\
\text{Cu} & \rightarrow \text{Cu}^{+2} + 2e^- & E^\circ_{1/2} = -0.34 \text{ V}
\end{align*}
\]
E°_{cell} \text{ an example}

Cd^{+2} + 2e^- \rightarrow \text{Cd} \quad E^°_{1/2} = -0.40 \text{ V}

\text{Cu} \rightarrow \text{Cu}^{+2} + 2e^- \quad E^°_{1/2} = -0.34 \text{ V}

\text{Cd}^{+2}(aq) + \text{Cu}(s) \rightarrow \text{Cd}(s) + \text{Cu}^{+2}(aq)

E^°_{cell} = -0.74 \text{ V}

\Delta G^0_{rxn} = -nFE^°_{cell} = -(2 \, e^- / \text{rxn}) \cdot (96485 \, C / \text{mol} \, e^-) \cdot (-0.74 \, J / C)

= 148kJ / \text{mole} – \text{rxn} \quad \text{(not spontaneous, not galvanic)}

When adding half reaction to get a net reaction (where n(e) drops out) then you can add the voltages. Warning: If n(e) does not drop out, you cannot just add voltages.
$E^\circ_{cell}$ and $K$

$\Delta G_{rxn} = -nFE_{cell}$

Under Standard conditions then:

$\Delta G^0_{rxn} = -nFE^0_{cell}$

Previously: $\Delta G_{rxn}^0 = -RT \ln K$

Therefore: $-nFE^0_{cell} = \Delta G^0_{rxn} = -RT \ln K$

$E^0_{cell} = \frac{RT}{nF} \ln K$

@ r.t. $T = 298.13K$  $RT = 2.477kJ/mole$

$\frac{RT}{F} = 2.57 \cdot 10^{-2} \frac{J/mole}{Coulombs/mole} = 25.7mV$

$\ln 10 = 2.303$  $25.7mV \cdot \ln 10 = 59mV$

$E^0_{cell} = \frac{25.7}{n} \ln K = \frac{59.1}{n} \log_{10} K \ mV$
The above relationship states that by measuring $E^\circ_{cell}$, we can determine $K$.

The above relationship illustrates that electrochemical cells are a venue in which thermodynamics is readily evident (an avatar).
$E^\circ_{cell}$ and $\Delta G^0_{rxn}$ and $K$

- Developing the “full picture”

$$\Delta G^0_{rxn} = -RT \ln K$$

$$\Delta G^0_{rxn} = -nFE^0_{cell}$$

$$E^0_{cell} = \frac{0.0591 V}{n} \cdot \log_{10} K$$

$$E^0_{cell} = \frac{RT}{nF} \cdot \ln K$$

It is important to see how all of these ideas interrelate.
An Example: determine $E^{\circ}_{\text{cell}}$ and $K$

- Balance, determine $E^{\circ}_{\text{cell}}$ and $K$ for the following:

$$S_4O_6^{2-} (aq) + Cr^{2+} (aq) \rightarrow Cr^{3+} (aq) + S_2O_3^{2-} (aq)$$

- Break the net reaction into its half reactions

$$2e^- + S_4O_6^{2-} \rightarrow 2S_2O_3^{2-}$$

$$Cr^{2+} \rightarrow Cr^{3+} + e^- \quad \times 2$$

$$S_4O_6^{2-} + 2Cr^{2+} \rightarrow 2Cr^{3+} + 2S_2O_3^{2-}$$
A Battery Example

• Determining $E^\circ_{\text{cell}}$

\[
2e^- + S_4O_6^{2-} \rightarrow 2S_2O_3^{2-} \quad E^\circ_{1/2} = 0.17 \text{ V}
\]
\[
2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^- \quad E^\circ_{1/2} = 0.50 \text{ V}
\]

\[
S_4O_6^{2-} + 2Cr^{2+} \rightarrow 2Cr^{3+} + 2S_2O_3^{2-} \quad E^\circ_{\text{cell}} = 0.67 \text{ V}
\]

From the two half reactions we see:

\[n = n(e) = 2\]

This voltage is NOT doubled
K for a Battery

• Determining K

\[ \text{S}_4\text{O}_6^{2-} + 2\text{Cr}^{2+} \rightarrow 2\text{Cr}^{3+} + 2\text{S}_2\text{O}_3^{2-} \]

\[ E^\circ_{\text{cell}} = 0.67 \text{ V} \]

\[ E^\circ_{\text{cell}} = \frac{(0.0257 \text{ V}) \ln(K)}{n} \]

\[ = \frac{(0.059 \text{ V}) \log K}{n} \]

\[ \frac{n(E^\circ_{\text{cell}})}{(0.059 \text{ V})} = \frac{2 (0.67 \text{ V})}{(0.059 \text{ V})} = 22.7 = \log K \]

\[ K = 10^{22.7} = 5 \cdot 10^{22} \]
Gibbs Energy from K

• Closing the loop (from the triangle relation of the full picture)

• Compute the Gibbs free energy of reaction:

\[ \Delta G_{rxn}^0 = -RT \ln K \]
\[ = -2.47 \cdot \ln(5 \cdot 10^{22}) \text{ kJ/mole} = -2.47 \cdot (22 \ln 10 + 0.7) \]
\[ = -127 \text{ kJ/mole} \]

\[ \Delta G_{rxn}^0 = -nF E_{cell}^0 = -2.96500 \cdot 0.67 \text{ J/mole} \]
\[ = -129 \text{ kJ/mole} \]

The numbers are the same by the two methods (with some round off differences). The reaction is highly spontaneous.