I. Relationship between Cell Potential ($\Delta E_{\text{cell}}$) and Gibbs Free Energy ($\Delta G$)

The flow of electrons arises from a potential difference, $\Delta E_{\text{cell}}$, between the electrodes in the circuit. $\Delta E_{\text{cell}}$ is known as cell voltage, and electromotive force (emf).

The overall free energy of the cell is related to the cell potential by

$$\Delta G_{\text{cell}} = -n \mathcal{F} \Delta E_{\text{cell}}$$

n = number of electrons

$\mathcal{F}$ = Faraday’s constant

For Standard State

$$\Delta G_{\text{cell}}^\circ = -n \mathcal{F} \Delta E_{\text{cell}}^\circ$$

$\Delta E_{\text{cell}}^\circ$ = cell potential (cell voltage) in which products and reactants are in their standard states

Units for $\Delta E$ is __________.

Example - Calculate $\Delta E_{\text{cell}}^\circ$ for $\text{Zn (s)} | \text{Zn}^{2+} (aq) \ || \ | \text{Cu}^{2+} (aq) | \text{Cu (s)}$

| Anode | Zn (s) $\Rightarrow$ Zn$^{2+}$ (aq) + 2e$^-$ |
| Cathode | Cu$^{2+}$ (aq) + 2e$^-$ $\Rightarrow$ Cu (s) |

$\Delta E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$

$\Delta E_{\text{cell}}^\circ$ = standard reduction potential for the couple at cathode minus standard reduction potential for the couple at anode

Look up Standard REDUCTION Potentials ($E^\circ$) in back of book

| Zn$^{2+}$ (aq) + 2e$^-$ $\Rightarrow$ Zn (s) $E^\circ$ = -0.7628 volts |
| Cu$^{2+}$ (aq) + 2e$^-$ $\Rightarrow$ Cu (s) $E^\circ$ = +0.3402 volts |

$\Delta E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$
Is the flow of electrons spontaneous?

\[ \Delta G^\circ_{\text{cell}} = -n \Delta E^\circ_{\text{cell}} \]

So, if \( \Delta E^\circ_{\text{cell}} \) is positive, \( \Delta G^\circ_{\text{cell}} \) will be negative.

Is a reaction spontaneous when \( \Delta G^\circ \) is negative?

What is the name of an electrochemical cell in which a \textbf{spontaneous} chemical reaction is used to generate an electric current?

What is the name of an electrochemical cell in which electrical energy provided by an external circuit is used to carry out \textbf{nonspontaneous} reactions?

**Summary**

Whether the cell operates spontaneously can be determined by \( \Delta E_{\text{cell}} \).

\((+\Delta E^\circ) = \text{spontaneous, since } +\Delta E^\circ \text{ means } -\Delta G^\circ\)

\( \Delta E_{\text{cell}} \) can be calculated from \textbf{Standard Reduction Potentials (E\textdegree)} of half-cell reactions.

### II. Meaning of standard reduction potential \( E^\circ \)

A large positive \( E^\circ \) means the element or compound is easy to reduce

\( \text{e.g. } F_2 (g) + 2e^- \rightarrow 2F^- \quad E^\circ = +2.87 \text{ volts (easy to add electrons to } F_2) \)

positive \( E^\circ \), negative \( \Delta G^\circ \), favorable

Is \( F_2 \) a good oxidizing agent?

A large positive \( E^\circ \) for \( F_2/F^- \) means the oxidized species of the couple is very oxidizing.
A large negative $E^\circ$ means the element or compound is hard to reduce

e.g. Li$^{+1}$ + e$^-$ \rightleftharpoons Li (s) \quad E^\circ = -3.045 \text{ volts}

(hard to add electrons to Li$^{+1}$)

negative $E^\circ$, positive $\Delta G^\circ$, not favorable

Is Li$^{+1}$ a good oxidizing agent?

Li (s) is a good __________________.

Li (s) reduces other elements or compounds. Li (s) gets oxidized.

For Li$^{+}$/Li with a large negative $E^\circ$, the reduced species of the couple is very reducing.

---

**IN THEIR OWN WORDS**

Prof. John Essigmann describes how oxidation reactions in our bodies are both essential for life and responsible for cell damage that can potentially lead to cancer. Research in the Essigmann lab focuses on studying how cells respond to toxins that cause oxidative damage to DNA.

---

**III. NERNST EQUATION**

An exhausted battery is a sign that the cell reaction has reached ________________.

At equilibrium, a cell generates __________ potential difference across its electrodes.

To understand this, we need to know how the cell potential changes with cell composition.

What do we know already about equilibrium and the components of a reaction?

We know that $\Delta G$ changes as the concentrations of the components change until equilibrium is reached, then $\Delta G = 0$.

$$\Delta G = \Delta G^\circ + RT \ln Q$$
What do we know about the relationship between $\Delta G^\circ$ and $\Delta E^\circ$?

$$\Delta G^\circ = -n\Phi \Delta E^\circ$$

Combining:

$$-n\Phi \Delta E = -n\Phi \Delta E^\circ + RT \ln Q$$

Dividing by $-n\Phi$:

$$\Delta E = \frac{\Delta E^\circ - RT \ln Q}{n\Phi}$$

(NERNST EQ.)

Example: Calculate $\Delta E$ (the cell potential, potential difference, emf) at 25 °C of a cell in which the concentration of Zn$^{2+}$ ions is 0.10 M and Cu$^{2+}$ is 0.0010 M.

Cu$^{2+}$ (aq)  + Zn (s) $\Rightarrow$ Zn$^{2+}$ (aq) + Cu (s)

Step 1: Calculate $\Delta E^\circ$ (Cell) from the $E^\circ$ for the half-reactions.

We already did this on page 1.

$\Delta E^\circ$(cell)  =  1.1030 V

Step 2: Calculate Q for Cu$^{2+}$ (aq)  + Zn (s) $\Rightarrow$ Zn$^{2+}$ (aq) + Cu (s)

Q =

Step 3: Find n

Step 4: Use the Nernst Eq.

$$\Delta E = \frac{\Delta E^\circ - RT \ln Q}{n\Phi}$$

$$\Delta E = 1.1030 V - \frac{(8.315 J K^{-1} mol^{-1})(298 K) \ln (1.0 \times 10^{-2})}{(2)(96485 Cmol^{-1})}$$

$$\Delta E = 1.1030 V - 0.0592 = +1.0438 V$$

NOTE: UNITS and CONSTANTS $1 \text{JC}^{-1} = 1 \text{V}$
At 25.00°C, \[ RT = \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K})}{(96485 \text{ Cmol}^{-1})} = 0.025693 \text{ V} \]

If you use log instead of ln \[ \Delta E = \Delta E^\circ - \frac{RT}{n\mathcal{F}} \log Q \] Use \((2.303)(0.025693) = 0.0592 \text{ V}\)

\[ \Delta E = \Delta E^\circ - \frac{0.025693 \text{ V}}{n} \ln Q \quad \text{OR} \quad \Delta E = \Delta E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \]

What about at EQUILIBRIUM?

\[ Q = ? \]

\[ \Delta G = ? \]

- \[ \Delta G = \Delta G^\circ + RT \ln Q \]
- \[ \Delta G^\circ = -RT \ln K \]
- \[ \Delta G^\circ = -n\mathcal{F}\Delta E^\circ \]

Combining:

- \[ -RT \ln K = -n\mathcal{F}\Delta E^\circ \]

OR:

- \[ \ln K = \frac{n\mathcal{F}\Delta E^\circ}{RT} \]

Can calculate _____ from standard potentials!

**Reduction potentials are not just important for batteries. Reduction potentials are important in biology too.**

**Question:** Vitamin B\(_{12}\) has a large negative reduction potential, so how is it reduced in the body?

Vitamin B\(_{12}\) needs to be reduced to be active. Proper functioning of an enzyme that requires vitamin B\(_{12}\) and folic acid is thought to be necessary for preventing heart disease and birth defects.

Where do you get vitamin B\(_{12}\) and folic acid in your diet?

Vitamin B\(_{12}\) is reduced by a protein called flavodoxin in a one electron process.

- \[ E^\circ \text{ for vitamin B}_{12} = -0.526 \text{ V} \]
- \[ E^\circ \text{ for flavodoxin} = -0.230 \text{ V} \]

Which is a better reducing agent?

Is the reduction of vitamin B\(_{12}\) by flavodoxin spontaneous?
Let’s calculate $\Delta E^\circ$ and $\Delta G^\circ$ from the standard reduction potentials

$E^\circ$ for vitamin B\textsubscript{12} is -0.526 V
$E^\circ$ for flavodoxin is -0.230 V

\[
\Delta E^\circ = E^\circ(\text{reduction}) - E^\circ(\text{oxidation})
\]
\[
= E^\circ(\text{vitamin B}\textsubscript{12}) - E^\circ(\text{flavodoxin})
\]
\[
= -0.526 \text{ V} - (-0.230 \text{ V}) =
\]

\[
\Delta G^\circ = -n\Delta E^\circ = - (1)(96485 \text{ Cmol}^{-1})(-0.296 \text{ V}) = +28.6 \text{ kJ/mol}
\]

Vitamin B\textsubscript{12} is a better reducing agent than flavodoxin. Vitamin B\textsubscript{12} should reduce flavodoxin not the other way around.

So why don't we all have heart disease?

How is the reaction driven forward? It is not spontaneous.

Answer: S-adenosylmethionine provides the energy to drive the reaction.

The $\Delta G^\circ$ for the cleavage of S-adenosylmethionine is -37.6 kJ/mol, which is greater than the +28.6 kJ/mol needed for the reduction reaction.

Net $\Delta G^\circ$ for coupled reaction =