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5.111 Principles of Chemical Science
Fall 2008

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Galvanic Cell is an electrochemical cell in which a _____ chemical reaction is used to generate an electric current.

Electrolytic Cell uses electrical energy provided by an external circuit to carry out _____ reactions.

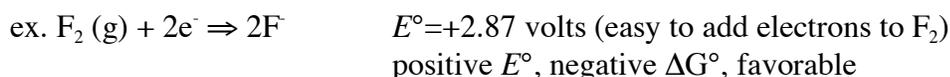
Summary

Whether the cell operates spontaneously can be determined by ΔE_{cell} . ((+) = spontaneous)

ΔE_{cell} can be calculated from the Standard Reduction Potentials (E°) of half-cell reactions.

Meaning of standard reduction potential E°

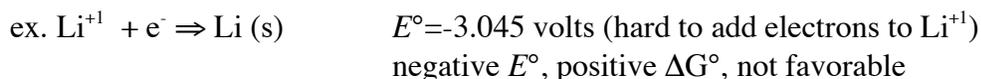
A large positive E° means the element or compound is easy to reduce



Is F_2 a good oxidizing agent?

A large positive E° means the oxidized species of the couple is very oxidizing.

A large negative E° means the element or compound is hard to reduce



Is Li^+ a good oxidizing agent?

A large negative E° means the reduced species of the couple is very reducing.

Example: What is ΔE° for the cell reaction: $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^- (\text{aq}) \Rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$?

balanced reaction at the cathode:

balanced reaction at the anode:

Standard Reduction Potentials are:

$$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.770 \text{ V}$$

$$E^\circ(\text{I}_2/\text{I}^-) = +0.535 \text{ V}$$

$$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ(\text{anode})$$

=

Is the reaction spontaneous?

Which is the better oxidizing agent: Fe^{3+} , I_2 ?

Which is the better reducing agent: I^- , Fe^{2+} ?

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? and how is the vitamin B_{12} reduced?

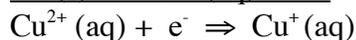
Today's material

Adding and Subtracting Half-Cell Reactions to Calculate ΔE° for a New Half-Cell Reaction

What if you need to know E° for the half-cell reaction: $\text{Cu}^{2+}(\text{aq}) + \text{e}^- \Rightarrow \text{Cu}^+(\text{aq})$, but it is not available in the Table in the book? However, values of E° for other reactions involving Cu are available.

One can add or subtract half-cell reactions with known E° to form the new half-cell reaction:

Half-cell reactions:



Standard Reduction Potentials are:

$$E^\circ(\text{Cu}^{2+}/\text{Cu}(\text{s})) = +0.340 \text{ V}$$

$$E^\circ(\text{Cu}^+/\text{Cu}(\text{s})) = +0.522 \text{ V}$$

and calculate the E° for that new half-cell reaction as follows:

$$\Delta G^\circ_{\text{new}} = \Delta G^\circ_{\text{reduction}} - \Delta G^\circ_{\text{oxidation}}$$

$$\text{or } -n_3 \mathfrak{S} E^\circ_3 (\text{new}) = -n_1 \mathfrak{S} E^\circ_1 (\text{reduction}) + n_2 \mathfrak{S} E^\circ_2 (\text{oxidation})$$

$$E^\circ_3 = \frac{n_1 E^\circ_1 (\text{reduction}) - n_2 E^\circ_2 (\text{oxidation})}{n_3}$$

$$E^\circ_3 = \frac{(2)(0.340\text{V}) - (1)(0.522\text{V})}{(1)} = 0.158 \text{ V} = E^\circ (\text{Cu}^{2+}/\text{Cu}^+)$$

NERNST EQUATION

An exhausted battery is a sign that the cell reaction has reached equilibrium. At equilibrium, a cell generates zero 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 ΔG 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 ΔG° and ΔE° ?

$$\Delta G^\circ = -n \mathfrak{S} \Delta E^\circ$$

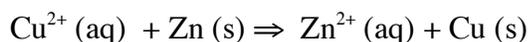
Combining:

$$-n \mathfrak{S} \Delta E = -n \mathfrak{S} \Delta E^\circ + RT \ln Q$$

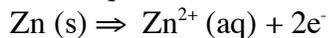
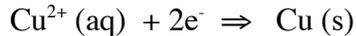
Dividing by $-n \mathfrak{S}$:

$$\Delta E = \Delta E^\circ - \frac{RT}{n \mathfrak{S}} \ln Q \quad (\text{NERNST EQ.})$$

Example: Calculate ΔE (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.



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



Standard Reduction Potentials

$$E^\circ(\text{Cu}^{2+}/\text{Cu}(\text{s})) = +0.340 \text{ V}$$

$$E^\circ(\text{Zn}^{2+}/\text{Zn}(\text{s})) = -0.7628 \text{ V}$$

$$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ(\text{anode})$$

$$=$$

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

$$Q =$$

Step 3: Find n

Step 4: Use the Nernst Eq.

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

$$\Delta E = 1.103 \text{ V} - \frac{(8.315 \text{ J K}^{-1}\text{mol}^{-1})(298 \text{ K})}{(2)(96485 \text{ Cmol}^{-1})} \ln (1.0 \times 10^2)$$

$$\Delta E = 1.103 \text{ V} - 0.0592 = +1.044 \text{ V}$$

NOTE: UNITS and CONSTANTS

$$1 \text{ J C}^{-1} = 1 \text{ V}$$

$$\text{At } 25.00^\circ\text{C}, \frac{RT}{\mathfrak{F}} = \frac{(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.15 \text{ K})}{(96485 \text{ Cmol}^{-1})} = 0.025693 \text{ V}$$

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

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

What about at EQUILIBRIUM?

$$Q = ?$$

$$\Delta G = ?$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -n\mathfrak{F}\Delta E^\circ$$

Combining:

$$-RT \ln K = -n\mathfrak{F}\Delta E^\circ$$

OR:

$$\ln K = \frac{n\mathfrak{F}\Delta E^\circ}{RT}$$

Can calculate K from standard potentials!

Now the answer to the biochemical question

How is vitamin B₁₂ reduced in the body? Vitamin B₁₂ is reduced by a protein called flavodoxin.

E° for vitamin B₁₂ is -0.526 V

E° for flavodoxin is -0.230 V

Is the reduction of vitamin B₁₂ by flavodoxin spontaneous?

$$\begin{aligned} \Delta E^\circ(\text{cell}) &= E^\circ(\text{reduction}) - E^\circ(\text{oxidation}) \\ &= E^\circ(\text{vitamin B}_{12}) - E^\circ(\text{flavodoxin}) \\ &= -0.526 \text{ V} - (-0.230 \text{ V}) = -0.296 \text{ V} \end{aligned}$$

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

Vitamin B₁₂ is a better reducing agent than flavodoxin. Vitamin B₁₂ should reduce flavodoxin not the other way around. So why don't we all have heart disease and megaloblastic anemia?

Answer: S-adenosylmethionine provides the energy to drive the reaction. The ΔG° for the cleavage of S-adenosylmethionine is -37.6 kJ/mol