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5.111 Principles of Chemical Science
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5.111 Lecture Summary #26
Oxidation/Reduction Lecture 3 and Nernst Equation

Topics: Adding and Subtracting Half-Cell Reactions, Chapter 12

From Friday's handout

Standard States and Cell Potentials

$\Delta G°_{cell} = -n\Im\Delta E°_{cell}$

$\Delta E°_{cell}$ = cell potential (cell voltage) in which products and reactants are in their standard states
Units for ΔE is volts.

Example - Calculate $\Delta E°_{cell}$ for

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

anode $Zn\ (s) \Rightarrow Zn^{2+}\ (aq) + 2e^- \Rightarrow Zn\ (s)$ (oxidation)

cathode $Cu^{2+}\ (aq) + 2e^- \Rightarrow Cu\ (s)$ (reduction)

$\Delta E°(\text{cell})$ = standard reduction potential for the couple at cathode minus standard reduction potential for the couple at anode

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

Look up Standard **REDUCTION** Potentials ($E°$) in back of book (measured against S.H.E)

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

$\Delta E°(\text{cell}) = E°(\text{cathode}) - E°\ (\text{anode})$
$E°\ (Cu^{2+}/Cu(s)) - E°(Zn^{2+}/Zn(s))$
$= 0.3402 - (-0.7628) = 1.103$ volts

Is the flow of electrons spontaneous?

$\Delta G°_{cell} = -n\Im\Delta E°_{cell}$

So, if $\Delta E°_{cell}$ is positive, $\Delta G°_{cell}$ will be negative.

Is a reaction spontaneous when $\Delta G°$ is negative?

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

ex. F_2 (g) + $2e^-$ $\Rightarrow$ $2F^-$ $E°$=+2.87 volts (easy to add electrons to F_2)
positive $E°$, negative $\Delta G°$, favorable

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

ex. Li^{+1} + e^- $\Rightarrow$ Li (s) $E°$=-3.045 volts (hard to add electrons to Li^{+1})
negative $E°$, positive $\Delta G°$, not favorable

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

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

Example: What is $\Delta E°$ for the cell reaction: $2Fe^{3+}$ (aq) + $2I^-$ (aq) $\Rightarrow$ $2Fe^{2+}$ (aq) + I_2 (s)?

balanced reaction at the cathode:

balanced reaction at the anode:

Standard Reduction Potentials are:
$E°(Fe^{3+}/Fe^{2+})$ = +0.770 V
$E°$ (I_2/I^-) = +0.535 V

$\Delta E°$(cell) = $E°$(cathode) - $E°$ (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 $\Delta E°$ for a New Half-Cell Reaction
What if you need to know $E°$ for the half-cell reaction: Cu^{2+} (aq) + e^- $\Rightarrow$ Cu^+ (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:
Cu^{2+} (aq) + $2e^-$ $\Rightarrow$ Cu (s)
$\underline{\text{Cu (s)} \Rightarrow Cu^+ \text{(aq)} + e^-}$
Cu^{2+} (aq) + e^- $\Rightarrow$ Cu^+ (aq)

Standard Reduction Potentials are:
$E°$ $(Cu^{2+}/Cu(s))$ = +0.340 V
$E°$ $(Cu^+/Cu(s))$ = +0.522 V

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

$\Delta G°_{new} = \Delta G°_{reduction} - \Delta G°_{oxidation}$

or $-n_3\Im E°_3\text{ (new)} = -n_1\Im E°_1\text{(reduction)} + n_2\Im E°_2\text{(oxidation)}$

$$E°_3 = \frac{n_1 E°_1\text{ (reduction)} - n_2 E°_2\text{ (oxidation)}}{n_3}$$

$$E°_3 = \frac{(2)(0.340\text{V}) - (1)(0.522\text{V})}{(1)} = 0.158\text{ V} = E°\ (Cu^{2+}/Cu^{+})$$

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 $\Delta G = 0$.

$$\Delta G = \Delta G° + RT \ln Q$$

What do we know about the relationship between $\Delta G°$ and $\Delta E°$?

$$\Delta G° = -n\Im\Delta E°$$

Combining:

$$-n\Im\Delta E = -n\Im\Delta E° + RT \ln Q$$

Dividing by $-n\Im$:

$$\Delta E = \Delta E° - \frac{RT}{n\Im} \ln Q \qquad \text{(NERNST EQ.)}$$

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.

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

Step 1: Calculate ΔE °(Cell) from the E° for the half-reactions.

Standard Reduction Potentials

Cu^{2+} (aq) + $2e^-$ $\Rightarrow$ Cu (s) — E° (Cu^{2+}/Cu(s)) = +0.340 V

Zn (s) $\Rightarrow$ Zn^{2+} (aq) + $2e^-$ — E° (Zn^{2+}/Zn(s)) = -0.7628 V

ΔE°(cell) = E°(cathode) - E° (anode)

=

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.

$$\Delta E = \Delta E° - \frac{RT}{n\Im} \ln Q$$

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

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

NOTE: UNITS and CONSTANTS **$1 \text{ JC}^{-1} = 1 \text{ V}$**

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

If you use log instead of ln $\Delta E = \Delta E° - \frac{RT}{n\Im} \log Q$ Use (2.303)(0.025693) = 0.0592 V

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

What about at EQUILIBRIUM?

Q = ?

ΔG = ?

$$\Delta G = \Delta G° + RT \ln Q$$
$$\Delta G° = - RT \ln K$$
$$\Delta G° = -n\Im\Delta E°$$

Combining:

$$-RT \ln K = -n\Im\Delta E°$$

OR:

$$\ln K = \frac{n\Im\Delta E°}{RT}$$

Can calculate K from standard potentials!

Now the answer to the biochemical question

How is vitamin B_{12} reduced in the body? Vitamin B_{12} is reduced by a protein called flavodoxin.

$E°$ for vitamin B_{12} is -0.526 V
$E°$ for flavodoxin is -0.230 V

Is the reduction of vitamin B_{12} by flavodoxin spontaneous?

$$\Delta E°(\text{cell}) = E°(\text{reduction}) - E°(\text{oxidation})$$
$$= E°(\text{vitamin } B_{12}) - E°(\text{flavodoxin})$$
$$= -0.526\text{ V} - (-0.230\text{ V}) = -0.296\text{ V}$$

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

Vitamin B_{12} is a better reducing agent than flavodoxin. Vitamin B_{12} 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 $\Delta G°$ for the cleavage of S-adenosylmethionine is -37.6 kJ/mol