5.111 Principles of Chemical Science

Fall 2008

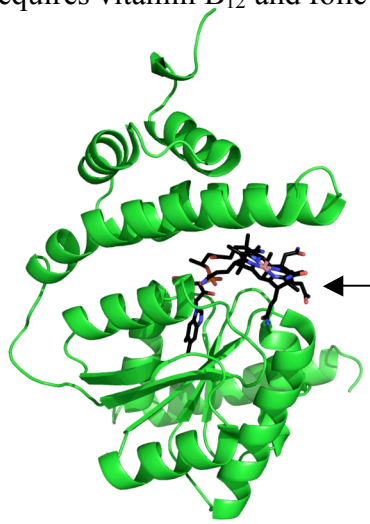
Chemical and Biological Oxidation/Reduction Reactions

See pages 1-3 of lecture 26 notes for the relationship between Gibbs free energy and cell potential. See pages 3-6 of Lecture 26 notes for adding and subtracting half-cell reactions.

Example from page 1 of Lecture 27 notes:

Reduction of Vitamin B_{12} in the Body

Proper functioning of an enzyme called methionine synthase is thought to be necessary for preventing heart disease and birth defects and for maintaining mental health. This enzyme requires vitamin B_{12} and folic acid.



Structure of the B_{12}-binding domain of methionine synthase.

The B_{12} molecule is shown in black.

(Figure from PDB: 1BMT)

THE VITAMIN B_{12} MUST BE REDUCED FOR THE ENZYME TO BE ACTIVE.

Where do you get vitamin B_{12} and folic acid in your diet?

Vitamin B_{12}: Red meat

Folic acid: Beer (Norwegian), Leafy green vegetables, Orange juice

Vitamin B_{12} has a large negative reduction potential, so how is it 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

Which is the better reducing agent, vitamin B_{12} or flavodoxin?

***Answer**: Vitamin B_{12} is a better reducing agent than flavodoxin, meaning B_{12} is harder to reduce.*

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

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

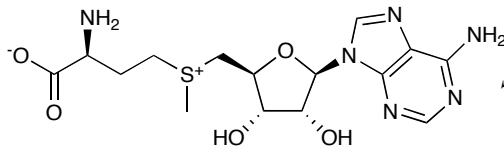
$\Delta G°$ = $-n\mathfrak{F}\Delta E°$ = -(1)(96485 $Cmol^{-1}$)(-0.296 V) = +28.6 kJ/mol

No. Reduction of vitamin B_{12} by flavodoxin is NOT spontaneous ($\Delta G°$ is positive).

Since vitamin B_{12} is a better reducing agent than flavodoxin, we might expect that vitamin B_{12} should reduce flavodoxin, not the other way around. So why don't we all have heart disease and megaloblastic anemia?

In other words, how is the B_{12} reduction reaction driven forward?

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



S-adenosylmethionine

The $\Delta G°$ for the cleavage of S-adenosylmethionine is -37.6 kJ/mol

What do you call a cell in which an unfavorable reaction is driven forward by applying energy?

Answer: *Electrolytic Cell*

(For more information on vitamin B_{12}: Lecture 23 includes a different example of an enzyme that requires B_{12}-binding, and Lecture 27 includes a chelation-complex example with the structure of vitamin B_{12}.)