Ch2/Ap2: Bioenergetics Section

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Introduction to bioenergetics.

The thermodynamics of biological energy production.

Kinetic aspects of bioenergetic processes.

The molecular and cellular organization of bioenergetic systems.

Photosynthesis

Respiration and ATP synthesis

Haber-Bosch process and biological nitrogen fixation
General references

Text: “Chemistry of the Environment”, esp. chaps 4, 15
photosynthesis and the web
http://www.life.uiuc.edu/govindjee/photoweb/

DOE genomes to life program
http://www.DOEgenomesToLife.org/

D.G. Nicholls and S.J. Ferguson  *Bioenergetics* 3
What is bioenergetics?

Bioenergetics is a way of understanding personality in terms of the body and its energetic processes. Bioenergetic Analysis is a form of therapy that combines work with the body and the mind to help people resolve their emotional problems and realize more of their potential for pleasure and joy in living.

http://www.bioenergetic-therapy.com/

energy changes in biological processes, specifically

“the mechanism by which energy made available by the oxidation of substrates, or the absorption of light, …(is) coupled to ‘uphill’ reactions such as the synthesis of ATP from ADP and Pi, or the accumulation of ions across the membrane”

why study bioenergetics?

biologically & technologically important process

catalyzed key scientific discoveries

implications for energy science/challenges
Nobel Prizes relevant to bioenergetics

chlorophyll and other pigments
- Richard Willstätter, Chemistry 1915
- Hans Fischer, Chemistry 1930
- R.B. Woodward, Chemistry 1965

AV Hill, Otto Meyerhof, Physiology or Medicine 1922
muscle metabolism

Otto Warburg, Physiology or Medicine 1931
respiration

Hans Krebs, Fritz Lipmann, Physiology or Medicine 1953
citric acid cycle (Krebs cycle)

Hugo Theorell, Physiology or Medicine 1955
oxidation enzymes

Melvin Calvin, Chemistry 1961
CO₂ assimilation in photosynthesis (Calvin cycle)

Peter Mitchell, Chemistry 1978
chemiosmotic theory

Hans Deisenhofer, Robert Huber, Hartmut Michel, Chemistry 1988,
x-ray structure of bacterial photosynthetic reaction center

Rudy Marcus, Chemistry, 1992
theory of electron transfer

Paul Boyer, John Walker, Chemistry 1997
mechanism of ATP synthesis

Rod MacKinnon, Peter Agre, Chemistry 2003
channel structure and mechanism

Images: [www.NNDB.com](http://www.NNDB.com)  
“Nobel Faces” by Peter Badge
Genomes to Life

Biological Solutions for Energy Challenges

Innovative Approaches Along Unconventional Paths

U.S. Department of Energy

DNA Sequence Data from Genome Projects

Support for the 21st Century

Genes and other DNA sequences contain instructions on how and when to build proteins.

Proteins perform many of life's most essential functions. To carry out their specific roles, they often work together in the cell as protein machines.

Identify Protein Machines

Goals:
- Explore Function in Microbial Communities
- Develop Computational Capabilities to Understand Complex Biological Systems
- Characterize Gene Regulatory Networks
- Produce and use energy
- Clean up the environment
- Sequester excess carbon
- Protect workers and the public
- Apply knowledge of microbial functional capabilities
- Many protein machines interact through complex, interconnected pathways. Analyzing these dynamic processes will lead to models of life processes.

URL: DOE.GenomesToLife.org
8/01
Energy Security and Climate Stabilization

U.S. Energy Security and Global Climate Stabilization

Complementary Goals

Energy conservation
Enzymes to replace energy-intensive thermo-chemical methods to process petroleum and develop new products

Energy resources
Biomass for liquid fuels
Biohydrogen for fuel cells

• Increased U.S. energy security
• Decreased adverse impact on global climate

Carbon management
Smokestack bioscrubbers
Biosequestration in photosynthetic terrestrial and aquatic organisms
Genomes to Life: Potential Impact on CO₂ Emissions

Reducing net CO₂ atmospheric emissions and dependence on imported oil

Conversion to fuels, electricity, and chemical products

Uses

CO₂ emissions
- Transportation
- Industrial
- Commercial
- Residential

Net atmospheric emissions

Increase due to GTL
Decrease due to GTL

Carbon from biomass

CO₂ uptake by plants

New energy sources
Hydrogen fuel cells: H₂ generated by biological systems from sunlight and water
Carbon stored in plants and soil microbes
Fossil feedstocks
- petroleum
- coal
- natural gas
Carbon stored in ocean microbial communities

Office of Biological and Environmental Research
Magnitude of biological energy metabolism

The basal metabolic rate of humans is $\sim 220 \text{ mm}^3 \text{ O}_2/\text{gm tissue/hr}$

$$\text{O}_2 + 4\text{H}^+ + 4 \text{e}^- \leftrightarrow 2\text{H}_2\text{O}$$

For a 70 kg person,

this corresponds to a rate of electrons through the respiratory pathway of $7.6 \times 10^{-4}$ moles e$^-$/sec

In terms of current flow, this is equivalent to 74 A
(with 1 Amp = 1 C/sec and 96,500 C/mole/e$^-$).

Power = current x voltage drop = 74 A x 1.1V = 84 watts.

(during strenuous exercise, wattage may be as high as 800 watts!)

daily energy consumption = $0.084 \times 24 = \sim 2 \text{ kW hrs} \sim 1700 \text{ Cal (kg)}$

total annual energy consumption (at rest) = 730 kW hrs
comparison to annual per capita electricity use

Physics Today, April 2002, pg. 39
ENERGY IN

light
chemical

organism
survival
growth
reproduction

ENERGY OUT

heat
work
waste
products

Bioenergetic Balance
photosynthesis

\[ n\text{H}_2\text{O} + n\text{CO}_2 + h\nu \leftrightarrow (\text{CH}_2\text{O})_n + n\text{O}_2 \]

acceptor \[ h\nu \] donor

A\(^-\) \rightarrow \text{use electrons to reduce CO}_2

D\(^+\) \leftarrow \text{replace electrons}

(oxidize H\(_2\)O to O\(_2\) in plants)

respiration

\[ \text{glucose} \ (C_6H_{12}O_6) + 6\text{O}_2 \leftrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} \]

\[ \Delta G^\circ = -2870 \text{ kJ/mole} \]
(sub)cellular organization

Buchanan, Gruissem, Jones
Biochemistry and Molecular Biology of Plants
*Rb. sphaeroides* photosynthetic reaction center (RC)

three subunits: L, M and H

view in plane of membrane

PDB IDs 2PRC; 1AIJ
*Rb. sphaeroides* photosynthetic reaction center (RC)

three subunits: L, M and H

view in plane of membrane

view down membrane normal

PDB IDs 2PRC; 1AIJ
organization of cofactors in the RC

Bchl - bacteriochlorophyll
Bph - bacteriopheophytin
Q - quinone

A branch
B branch

organization of photosynthetic membranes
incident solar radiation ~1 photon/RC/sec
the cycling time for the RC is ~ $10^{-3}$ sec;
light harvesting/antennae complexes to funnel light to the RC
represent most of the “2480” chlorophylls / photosynthetic unit
organization of photosynthetic membranes
incident solar radiation $\sim 1$ photon/RC/sec
the cycling time for the RC is $\sim 10^{-3}$ sec;
light harvesting/antennae complexes to funnel light to the RC represent most of the “2480” chlorophylls / photosynthetic unit
organization of photosynthetic electron transfer assembly

http://www.bio.ic.ac.uk/research/barber/photosystemII.html
Quinones: the final acceptor in bacterial RCs
lipid soluble carriers of electrons and protons

oxidized quinone
(Q$_{10}$)

semiquinone
(can be protonated)

hydroquinone

Coenzyme Q10, Source Naturals, 200 mg, 60 Softgels

Label information:

Coenzyme Q10 is a crucial component in the primary energy production cycle. Research indicates that supplementation with this nutrient may support normal heart function, provide antioxidant protection and maintain the health of the gums.

Respiratory chain complexes

- Complex I (NADH ubiquinone oxidoreductase)
- Complex II (succinate quinone oxidoreductase)
- Complex III (cytochrome bc₁)
- Complex IV (cytochrome c oxidase)

H⁺ flow:
- (-) matrix to (+) cytosol
- ATP synthase: ADP + Pi → ATP
- F₁ ATP synthase
- F₀ ATP synthase

Electron transfer:
- NADH → NAD⁺
- succinate → fumarate
- QH₂ → Q
- O₂ → H₂O
- Cytochrome c
nicotinamide adenine dinucleotide (NAD)
(derived from niacin)
brings in reducing equivalents
from substrate oxidation

\[
\begin{array}{c}
\text{NAD(P)}^+ \\
\text{NAD(P)H}
\end{array}
\]
ATP - adenosine triphosphate - phosphoanhydride
central energy currency of cells (Lipmann)
energy released during respiration/ photosynthesis is captured by ATP synthesis through the process of “oxidative phosphorylation”

\[ \text{ATP} + \text{H}_2\text{O} \rightleftharpoons \text{ADP} + \text{P}_i \quad \Delta G^\circ = -30 \text{ kJ/mole} \]
How does oxidative phosphorylation occur?

direct chemical coupling??

substrate level phosphorylation in glycolysis
In spite of exhaustive searches, no high energy phosphorylated intermediates such as 1,3 diphosphoglycerate were ever found...

Important clue: Oxidative phosphorylation can only take place in intact membranes—damaged mitochondria cannot make ATP. This was “curious”, since membrane integrity shouldn’t influence stability of an intermediate.

This situation led to proposal (“the chemiosmotic theory”) by Peter Mitchell in 1961 that energy released during respiration or photosynthesis is not stored in high energy chemical intermediate, but rather in a proton gradient.
chemiosmotic principles

Figure 1.3  Proton circuits and electrical circuits are analogous. A simple electrical circuit comprising battery and light bulb is analogous to a basic proton circuit. Voltage ($\Delta p$ equivalent to $V$), current ($J_{H^+}$ equivalent to $I$) and conductance $C_{M}H^+$ (equivalent to electrical conductance – reciprocal ohms) terms can be derived. Short-circuits have similar effects and more complex circuits with parallel batteries can be devised to mimic the multiple proton pumps in the mitochondrion (see Chapter 4).

Nichols and Ferguson, Bioenergetics 3
ATP synthesis - molecular motor

Paul Boyer and John Walker
movie of single F1 ATP synthase with fluorescent actin label

http://www.res.titech.ac.jp/~seibutu/projects/fig/f1rot_2.mov
biosynthetic processes:

use ATP and reductive power generated during respiration and photosynthesis to build molecules of the cell, ie, biomass

Alberts et al.
Essential Cell Biology
Biological Nitrogen Cycle

- NO\textsubscript{3} → nitrite oxidase → NO\textsubscript{2} → hydroxylamine oxidoreductase → NH\textsubscript{2}OH
- NH\textsubscript{2}OH → ammonia monooxygenase → NH\textsubscript{4}\textsuperscript{+}
- NH\textsubscript{4}\textsuperscript{+} → ANAMOX process → N\textsubscript{2}O → N\textsubscript{2} → nitrogenase
- NO → copper nitrite reductase → NO\textsubscript{2} → nitric oxide reductase → N\textsubscript{2}O → nitrous oxide reductase
- NO\textsubscript{3} → assimilatory nitrate reductase
- NO\textsubscript{2} → cytochrome cd\textsubscript{1} nitrite reductase
- NO\textsubscript{2} → cytochrome c nitrite reductase
- NH\textsubscript{4}\textsuperscript{+} → assimilatory nitrite reductase
Thermodynamic foundations of bioenergetics

energy inputs:

photons

reduced chemicals

photon energy:

\[ E = h \nu = \frac{hc}{\lambda} \]

for a single photon

\[ = Nh\frac{c}{\lambda} \]

for a mole of photons (1 einstein)

\[ = 1.20 \times 10^5/\lambda \text{ kJ mol}^{-1} = (\lambda \text{ in nm}) \]

\[ = 1.24 \times 10^3/\lambda \text{ eV} \]

for \( \lambda = 780 \text{ nm}, E = 154 \text{ kJ mol}^{-1} = 1.6 \text{ eV} \)
(A) Chlorophylls

Absorption

Wavelength (nm)

Chlorophyll a
Chlorophyll b
Bacteriochlorophyll a

Visible solar spectrum

400 500 600 700 800

3.1 eV

1.6 eV

(B) Other photosynthetic pigments

Absorption

Wavelength (nm)

Carotenoids
Phycocyanin
Phycoerythrin
Visible solar spectrum

400 500 600 700 800

3.1 eV

1.6 eV

Figure 12.6

(A) Absorption spectra of chlorophylls. The absorption spectra of pigments dissolved in nonpolar solvents are shown for chlorophyll a and b and bacteriochlorophyll a. The visible region of the solar spectrum is also diagrammed. Note that the spectra of these pigments show substantial shifts in absorbance in vivo, where they are associated with specific proteins. (B) Absorption spectra of other photosynthetic pigments. The absorption spectrum of the carotenoids is for pigments dissolved in nonpolar solvents; the remaining spectra are for pigments in aqueous solution. UV, ultraviolet; IR, infrared.
Gibbs Free Energy, $G$

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G$, $\Delta H$ and $\Delta S$ are the changes in Gibbs free energy, enthalpy and entropy, respectively.

$\Delta G$ describes the maximum amount of non-expansion work that is available in a process at constant $T$, $P$

for a spontaneously occurring process at constant $T$, $P$

$$\Delta G < 0$$

and at equilibrium, $\Delta G = 0$
for a reacting system system with

\[ \nu_1A + \nu_2B + \ldots \leftrightarrow \nu_iP + \nu_{i+1}Q + \ldots \]

\[ \Delta G = \Delta G^\circ + RT \ln \frac{\prod c_i^{\nu_i} \text{(products)}}{\prod c_j^{\nu_j} \text{(reactants)}} \]

at equilibrium, \( \Delta G = 0 \), so that

\[ \Delta G^\circ = -RT \ln K_{eq} \]

\[ K_{eq} = \frac{\prod c_i^{\nu_i} \text{(products)}}{\prod c_j^{\nu_j} \text{(reactants)}} \]

\( \left\{ \begin{array}{l} \nu_i = \text{stoichiometric coefficients} \\ c_i = \text{equilib. concentrations} \end{array} \right\} \)

standard state convention in biochemical systems (\( \Delta G^\circ' \));

1M except for water (unity) and (H\(^+\))=10\(^{-7}\) M
ΔG for ATP hydrolysis under physiological conditions

While ΔG° for ATP hydrolysis at pH 7 is -30 kJ/mol, under physiological conditions, the actual ΔG is more negative, due to the non-equilibrium concentrations of reactants (high) and products (low):

For the reaction

\[ \text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{P}_i \]

\[ \Delta G = \Delta G + RT \ln \left( \frac{(\text{ADP})(\text{P}_i)}{(\text{ATP})} \right) \]

With

- ATP = 0.01 M (10 mM)
- ADP = 0.0001 M (0.1 mM)
- Pi = 0.01 M (10 mM)

\[ \Delta G = -30 + 2.5 \ln \left( \frac{10^{-6}}{10^{-2}} \right) = -30 - 23 = -53 \text{ kJ/mole} \]