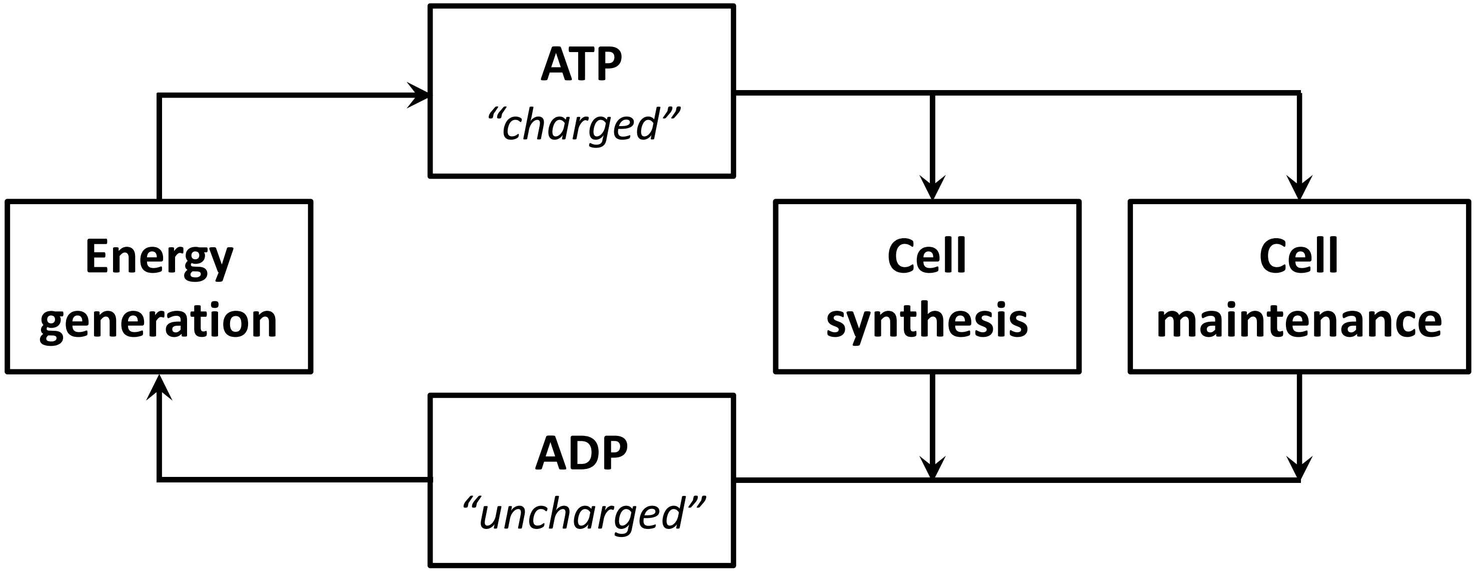
Bacterial energetics

Today’s lecture

- Bacterial energetics – overview
- Gibbs free energy of reaction
- Correlation of reaction energetics and yield coefficient

Bacterial energetics

- Microorganisms carry out redox reactions to obtain energy for growth and cell maintenance



ATP
"charged"

Energy generation

Cell synthesis

Cell maintenance

ADP
"uncharged"

Energetics and bacterial growth

- The bacterial cells grow more rapidly when:
  - More energy can be obtained by oxidation of (an e^- equivalent of) an e^- donor
  - More energy can be obtained by reduction of (an e^- equivalent of) an e^- acceptor
  - When conditions are favorable
    - abundance of e^- donor, e^- acceptor, nutrients, etc.
    - low concentration of inhibiting compounds

  → rapid utilization of substrates

Energetics and bacterial growth

- Consider:

$$Y_n = Y - b\frac{X_a}{-dS/dt}$$

  - Larger Y_n when Y >> b: favorable e^- donor and acceptor
  - Larger Y_n when X_a << -dS/dt: favorable conditions for substrate utilization

Gibbs free energy: standard conditions

- "Standard" free energy
  - ΔG^0, free energy at 25°C, 1 atm, and unit activity for any chemicals involved
  - $\Delta G^{0\prime}$, standard free energy adjusted to pH=7

ex) $\frac{1}{4}O_2 + H^+ + e^- = \frac{1}{2}H_2O$

ΔG^0 is for $\{O_2\} = P_{O_2} = 1\,atm$
$\{H^+\} = 1$ (pH = 0)
$\{H_2O\} = 1$

ΔG^0 is for $\{O_2\} = P_{O_2} = 1\,atm$
ph=7 ($\{H^+\} = 10^{-7}$)
$\{H_2O\} = 1$

$\{H_2O\} = 1$ applies to any dilute aqueous solutions

Free energy of formation, ΔG_f

- Gibbs free energy that accompanies the formation of 1 mole of the substance from its component elements

Gibbs free energy change of reaction

- Free energy change of reaction, ΔG_r

$$\sum\left[\left(sum\ of\ product\ \Delta G_f\right) - \left(sum\ of\ reactant\ \Delta G_f\right)\right]$$

For a generic reaction written as

$$0 = \sum_{i=1}^{n} v_{ir} A_i$$

v_{ir} *= stoichiometric coefficient, (-) for reactants, (+) for products*

A_i *= reaction constituent, reactants or products*

The ΔG_r *can be written as*

$$\Delta G_r = \sum_{i=1}^{n} v_{ir} \Delta G_f$$

Reaction free energy

Q1: Calculate the standard free energy adjusted pH 7 for the half reaction of 2-chlorobenzoate formation as given below.

$$\frac{1}{28}HCO_3^{-}(aq) + \frac{3}{14}CO_2(g) + \frac{1}{28}Cl^{-}(aq) + \frac{29}{28}H^{+}(aq) + e^{-} \rightarrow \frac{1}{28}C_6H_4ClCOO^{-}(aq) + \frac{13}{28}H_2O(l)$$

Use the following values of free energy of formation (in textbook Appendix A):

Species	HCO_3^-(aq)	CO_2(g)	Cl^-(aq)	H^+(aq, 10^{-7})	$C_6H_4ClCOO^-$(aq)	H_2O(l)
ΔG_f @ 25^oC (kJ/mole)	-586.85	-394.36	-31.35	-39.87	-237.9	-237.18

Reaction free energy

Q2: Calculate the standard free energy adjusted pH 7 for overall energy reaction with ethanol as an e^- donor and oxygen as an e^- acceptor. Use the half reactions listed in Table 2.2 and 2.3.

Reaction free energy

- For nonstandard conditions,

$$\Delta G_r = \Delta G_r{}^0 + RT\sum_{i=1}^{n} v_{ir} ln a_i$$

a_i = activity of constituent A_i

R = gas constant, $8.314 \times 10^{-3}\ kJ/mole - K$

T = absolute temperature, K

Caution:

- v_{ir} is negative for reactants and positive for products
- $\Delta G_r{}^0$ is for standard conditions -- pH=0

From $\Delta G_r{}^{0\prime}$, we can calculate $\Delta G_r{}^0$ by:

$$\Delta G_r{}^0 = \Delta G_r{}^{0\prime} - \mathrm{RT} v_{H^+} ln[10^{-7}]$$

Reaction free energy

Q3: Calculate the free energy of reaction for aerobic ethanol degradation at the following conditions: T = 20°C, pH = 5.0, [C_2H_5OH] = 2×10^{-3} M, $P_{CO2} = 3 \times 10^{-4}$ atm, $P_{O2} = 0.21$ atm.

Yield coefficient and reaction energetics

- The energy generated by energy reactions is spent to make ATP
- ATP is consumed to drive cell synthesis or cell maintenance
- True yield (Y) or f_s^0 does not involve costs for cell maintenance
- Cell synthesis involves energy loss (bacteria are not 100% efficient engines!) to synthesize C source to an intermediate compound, and then the intermediate compound to cells

Yield coefficient and reaction energetics

- Energy required to convert carbon source to pyruvate, ΔG_p (heterotrophic bacteria, ammonia as N source):

$$\Delta G_p = 35.09 - \Delta G_c{}^{0\prime}$$

(in kJ/e^- eq)

35.09 = reaction free energy for formation of pyruvate from CO_2

$\Delta G_c{}^{0\prime}$ = reaction free energy for formation of carbon source from CO_2

- Energy required to convert pyruvate to cells, ΔG_{pc} = 18.8 kJ/e^- eq

  (estimated value for a cell formula of $C_5H_7O_2N$ using NH_4^+ as a N source)

Yield coefficient and reaction energetics

- Energy required for cell synthesis from the carbon source, ΔG_s:

$$\Delta G_s = \frac{\Delta G_p}{\varepsilon^n} + \frac{\Delta G_{pc}}{\varepsilon}$$

ε = energy transfer efficiency

n = -1 for $\Delta G_p < 0$ (C-source is at higher energy state than pyruvate);
+1 for $\Delta G_p > 0$ (C-source is at lower energy state than pyruvate)

- If energy for cell maintenance is neglected (situation for true yield, *Y*, and f_s^0):

$$A\varepsilon\Delta G_r + \Delta G_s = 0$$

A = e$^-$ equivalent of e$^-$ donor used for energy production per equivalent of cells formed

Yield coefficient and reaction energetics

- Solving for A:

$$A = -\frac{\Delta G_p/\varepsilon^n + \Delta G_{pc}/\varepsilon}{\varepsilon \Delta G_r}$$

- From A, we can calculate $f_s{}^0$ and $f_e{}^0$ as:

$$f_s{}^0 = \frac{1}{1+A} \qquad f_e{}^0 = 1 - f_s{}^0 = \frac{A}{1+A}$$

- Energy transfer efficiency, ε
  - 55-70% under optimal conditions
  - Use 0.6 for ordinary cases

Yield coefficient and reaction energetics

Q4: Estimate f_s^0 and Y for aerobic oxidation of acetate assuming ε=0.4 and 0.6 at standard conditions except for a pH of 7.0. Ammonia is available for cell synthesis.