CELL THERMODYNAMICS AND ENERGY METABOLISM

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Keywords: thermodynamics, energy production, conservation, membrane, solute transport, energy metabolism, enzyme catalysis

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Summary

The most fundamental property of living cell systems is their ability to utilize and transform energy involving thousands of individual and enzyme-catalyzed chemical reactions. Since every chemical reaction involves a loss or gain of electrons, the amount of energy released or used depends on the oxidation-reduction potential difference or distance between the electron donor (oxidized compound) and electron acceptor [reduced compound]. In order to maintain its integrity, gain and loss of energy must be balanced via a controlled flow [electron transport] and energy transformation (ADP $\leftrightarrow$ ATP), which follows the laws of thermodynamics.

On the basis of electron donor and electron acceptor availability, four modes of energy production are recognized, namely photosynthesis, aerobic respiration, anaerobic respiration and fermentation.

The energy transformations are also vital for the transport of solutes along pH and electrical gradients across the otherwise impermeable cellular membrane.

1. Introduction

One of the most fundamental properties of living cell systems is their ability to utilize and transform energy. This energy occurs in a number of forms:

- Mechanical Energy is developed during cellular movement, beating of flagella, re-organization of intracellular structures such as mitochondria, and alteration of cell shape;
- Electrical Energy is produced when electrons move from one place to another, usually expressed as a flow of current between two points due to a difference in voltage;
- Electromagnetic Energy occurs in the form of radiation, and in biology the most significant is that from visible or near-visible light, such as radiation from the sun for photosynthetic organisms. Some organisms release energy and glow, which is referred to as bioluminescens. They produce light energy;
- Chemical Energy is the energy that can be released from chemical reactions;
- Thermal Energy or heat is produced as part of the normal energy transformation processes and occurs as waste energy released into the surroundings;
- Atomic Energy is contained within the structure of atoms themselves and is released in the form of atomic radiation, which cannot be utilized by living organisms.

Since growth can be defined as the orderly increase of all chemical components, it is the chemical form of energy, which is of greatest importance for the understanding of microbial growth and metabolism.

2. Concepts of Thermodynamics

Cell metabolism consists of thousands of individual chemical and enzyme-catalyzed chemical reactions. These chemical reactions in living organisms occur in characteristically organized sequences, called metabolic pathways (see also *Cell metabolism*). There are two main types of metabolic pathways:

- Pathways which lead from large (low oxidative state) to smaller molecules (high oxidative state), which are called catabolic pathways or catabolism
- Pathways which lead from small (high oxidative state) to large molecules (low oxidative state) essential for the formation of cellular material, which are referred to as anabolic or biosynthetic pathways, or anabolism.

The main concept of catabolism is therefore to provide the cell with small molecules or precursors suitable for biosynthesis of all major chemical constituents of the living cell with reductant and energy to carry out these endergonic and reducing reactions leading towards compounds of low oxidative state (Figure 1). Whereas all catabolic pathways are oxidative and thus energy producing, the biosynthetic pathways are reductive and energy consuming. Metabolism consists therefore entirely of energy transformation and

transfer mechanisms, which are based on thermodynamics.

2.1. First Law of Thermodynamics

The amount of energy involved in a chemical reaction is expressed in terms of gain or loss of energy during the reaction. The First Law of Thermodynamics is the law of conservation of energy and states that the total amount of energy in nature is constant. This means that, if heat [q] is added to a system of a given energy content, it must appear as a change in the internal energy [ΔE] of the system or in the total work performed by the system on the surrounding [w]

$$q \; = \; \Delta E \; + \; w' \tag{1}$$

$$\Delta E \; = \; q \; - \; w' \tag{2}$$
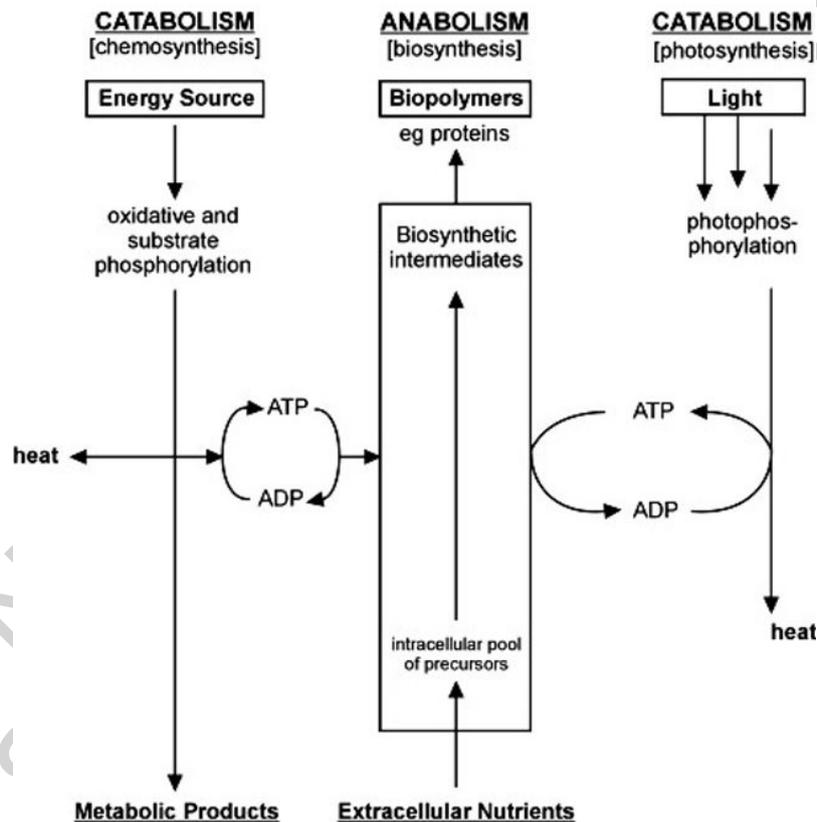
Figure1. Generalized scheme for metabolic energy formation and usage
(adapted from Doelle 1994b).

Such an addition of heat results in many instances in a change of volume [ΔV] at a constant pressure [P]

$$q \; = \; \Delta E \; + \; P\Delta V \; + \; w' \tag{3}$$

Whereby the expression $\Delta E + P\Delta V$, representing the change of the heat content or enthalpy, can be replaced by ΔH

$$\Delta H \quad = \quad \Delta E \quad + P\Delta V \tag{4}$$

$$= \quad q - w' \tag{5}$$

At any temperature, $P\Delta V = nRT$, where n represents the number of moles and R is the gas constant [= 1.987 cal.moldegree^{-1}] with T signifying the absolute temperature

$$\Delta H \quad = \quad \Delta E \quad + \quad nRT \tag{6}$$

This expression reveals that each chemical reaction proceeds to completion with a definite heat of reaction that is quantitatively related to the number of molecules reacting. The energy unit for its measurement is the calorie, which is defined as the quantity of heat energy necessary to raise the temperature of 1 g water by 1°C. One calorie is equal to 4.184 joules.

Example:

$$C_6H_{12}O_6 \rightarrow 6\ CO_2 + 6\ H_2O$$

$$\Delta H = -673\ kcal = -2,815.8\ kJ/mol$$

The negative sign indicates an exergonic reaction.

2.2. Second Law of Thermodynamics

Whereas the first law of thermodynamics implies only that there is a quantitative correspondence between different kinds of energy and that the energy content in nature is constant, the Second Law of Thermodynamics states that all physical and chemical processes proceed in such a direction that the randomness or entropy of the universe increases to the maximum possible, at which point there is an equilibrium. Since the entropy has the symbol S,

$$\Delta S \quad = \quad q/T \tag{7}$$

$$q \quad = \quad T\Delta S \tag{8}$$

If one combines the equations of the first and second law of thermodynamics,

$$\Delta H \quad = \quad T\Delta S \quad - \quad w' \tag{9}$$

In considering these thermodynamic relationships one should always be aware that the main interest in biological reactions is not in reactions at equilibrium, but in those

proceeding in the direction that approaches equilibrium. The tendency to seek the position of maximum entropy is the driving force of all processes, and heat is either given up or absorbed by the surrounding system to allow the system plus its surroundings to reach the state of maximum entropy.

These changes in heat and entropy are related by the free energy, ΔG

$$\Delta G \ = \ \Delta H \ - \ T \Delta S \tag{10}$$

and since

$$\Delta H \ = \ T \Delta S \ - \ w',$$

$$\Delta G \ = \ -w' \tag{11}$$

which expresses the energy released that is available to do useful work. The determination of ΔG depends on accurate measurements of either the equilibrium constant, K, of a reversible reaction or its electromotive force. The equilibrium constant is very difficult to determine, since often no adequate analytical methods are available to analyze the reactants and product concentrations.

2.3. Free Energy

Since metabolism consists of sequences of oxidations and reductions, the measurement of the electromotive force is the choice for establishing ΔG.

This electromotive force is the algebraic difference of the potentials of two half-cells. In order to understand this definition, it is necessary to realize that energy-yielding reactions within the cell are of the nature of oxidations. An oxidation is generally defined as the loss of electrons and reduction as the gain of electrons

$$H_2 \ + \ 2e^- \ \leftrightarrow \ 2H^+$$

Electrons released by an oxidation MUST be accepted by an oxidizing agent, which itself will be reduced. Such a transfer of electrons, according to modern theory, establishes an electric current, since the electron donor possesses a characteristic electron affinity. It should therefore be possible to obtain direct proof of the transfer of electricity in oxidation-reduction reactions under suitable experimental conditions. This transfer could be a quantitative measure of the tendency of substances to donate or accept electrons and thus a means for calculating free energy changes for oxidation-reduction reactions. This quantitative measure is termed an oxidation-reduction potential.

The measured potential difference [E_h] of an oxidation-reduction system is expressed by the NERNST equation

$$E_h = E_0 + \frac{RT}{nF} \ln \frac{[A_{ox}]}{[A_{red}]} \tag{12}$$

where E_0 is the standard electrode potential, R is the gas constant (= 8.314 J degree^{-1} mol^{-1}), n represents the number of electron involved in the reaction, F is the Faraday constant (= 96,494 coulomb) necessary to convert one equivalent of ions, and $[A_{ox}]$ and $[A_{red}]$ are the activities of the oxidized and reduced form of the oxidation-reduction system.

The standard electrode potential $[E_0]$ is the potential of an electrode in equilibrium with a unity activity of its ions. This value is characteristic for each oxidation-reduction system and gives a measure of the relative ability of that system to accept or donate electrons in oxidation-reduction reactions.
The free energy change associated with an oxidative reaction may now be calculated from the standard electrode potentials of the two reacting systems. For this, the NERNST equation for the two systems has to be incorporated into the standard free energy equation

$$\Delta G = RT \ln K \quad \Delta E_0 = (RT/nF) \ln K$$

$$nF\Delta E_0 = RT \ln K \tag{13}$$

therefore

$$-\Delta G = nF\Delta E_0 \tag{14}$$

Let us demonstrate these calculations on an example:

malate + cyt.c →oxalacetate + cyt. C

malate/oxalacetate has a $\Delta E_0 = - 0.17V$

cyt. c_{ox}/cyt. c_{red} has a $\Delta E_0 = + 0.22V$

therefore,

$$\begin{aligned}
\Delta G &= -nF\Delta E_0 \\
&= -2 \times 96,500 \times [0.22 - (-0.17V)] \\
&= -75.34 \quad kJmol^{-1}
\end{aligned}$$

Since electrons move only to a more positive redox system, the greater the difference between the systems, the greater is the oxidizing ability of the system. Energy is released in direct proportion to the difference in E_0 values.

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Biographical Sketch

Horst W.Doelle, born in 1932, studied biology at the University of Jena (1950-1954). He studied for his doctorate at University of Goettingen [1955-1957] on antibiotic production. After receiving his doctorate, he worked in the Wine and brewing industry in Germany before taking up an appointment with CSIRO in Australia in 1960. After 4 years wine research, he took up the challenge to build up microbial physiology and fermentation technology at the Department of Microbiology at the University of Queensland in Brisbane. He received his Doctor of Science in 1976 and his Doctor of Science honoris causa in 1998. He perticipated and conducted numerous training courses in developing countries. After 29 years teaching he retired in 1992. His research area was regulation of anaerobic/aerobic metabolism, microbial technology (Zymomonas ethanol technology) and socioeconomic biotechnology using microorganisms for waste management.