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Notes on -“ Biological oxidation ”

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Biological oxidation

Introduction

Bioenergetics is the part of biochemistry concerned with the energy involved in making and breaking of chemical bonds in the molecules found in biological organisms. It can also be defined as the study of energy relationships and energy transformations and transductions in living organisms.

Biological oxidation is the combination of **oxidation**-reduction transformations of substances in living organisms. **Oxidation**-reduction reactions are those which take place with a change in the **oxidation** state of atoms through the redistribution of electrons between them.

or

Biological oxidation is catalysed by enzymes which function in combination with coenzymes and/or electron carrier proteins.

The differences between biological oxidation and combustion

	Biologic oxidation	combustion
Reaction conditions	Reaction occurs at 37°C, neutral pH, water involved	High temperature and dry conditions
Reaction models	Reaction is under the catalysis of enzymes, O ₂ accepts 2 electrons and then combines with proton to form water, CO ₂ is formed by decarboxylation of substances.	Reaction occurs break out suddenly without catalysis, hydrogen and oxygen combine directly to form water and CO ₂ .
Type of energy liberated	During the reaction, energy is liberated stepwise, part energy is accumulated as chemical energy for living processes, part energy is released as heat to keep body temperature.	All energy bursts out as the form of heat and light.



Free energy

A process will only happen spontaneously, without added energy, if it increases the entropy of the universe as a whole (or, in the limit of a reversible process, leaves it unchanged) – this is the Second Law of Thermodynamics. But to me at least, that's kind of an abstract idea. How can we make this idea more concrete and use it to figure out if a chemical reaction will take place?

Basically, we need some kind of metric that captures the effect of a reaction on the entropy of the universe, including both the reaction system and its surroundings. Conveniently, both of these factors are rolled into one convenient value called the Gibbs free energy.

The Gibbs free energy (G) of a system is a measure of the amount of usable energy (energy that can do work) in that system. The change in Gibbs free energy during a reaction provides useful information about the reaction's energetics and spontaneity (whether it can happen without added energy). We can write out a simple definition of the change in Gibbs free energy as:

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

In other words, ΔG is the change in free energy of a system as it goes from some initial state, such as all reactants, to some other, final state, such as all products. This value tells us the maximum usable energy released (or absorbed) in going from the initial to the final state. In addition, its sign (positive or negative) tells us whether a reaction will occur spontaneously, that is, without added energy.

When we work with Gibbs free energy, we have to make some assumptions, such as constant temperature and pressure; however, these conditions hold roughly true for cells and other living systems.

Gibbs free energy, enthalpy, and entropy

In a practical and frequently used form of Gibbs free energy change equation, ΔG is calculated from a set values that can be measured by scientists: the enthalpy and entropy changes of a reaction, together with the temperature at which the reaction takes place.

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

Let's take a step back and look at each component of this equation.

ΔH is the enthalpy change. Enthalpy in biology refers to energy stored in bonds, and the change in enthalpy is the difference in bond energies between the products and the reactants. A negative ΔH means heat is released in going from reactants to products, while a positive ΔH means heat is absorbed. (This interpretation of ΔH assumes constant pressure, which is a reasonable assumption inside a living cell).

ΔS is the entropy change of the system during the reaction. If ΔS is positive, the system becomes more disordered during the reaction (for instance, when one large molecule splits into several smaller ones). If ΔS is negative, it means the system becomes more ordered.

Temperature (T) determines the relative impacts of the ΔS and ΔH terms on the overall free energy change of the reaction. (The higher the temperature, the greater the impact of the ΔS term relative to the ΔH term.) Note that temperature needs to be in Kelvin (K) here for the equation to work properly.

Reactions with a negative ΔG release energy, which means that they can proceed without an energy input (are spontaneous). In contrast, reactions with a positive ΔG need an input of energy in order to take place (are non-spontaneous). As you can see from the equation above, both the enthalpy change and the entropy change contribute to the overall sign and value of ΔG . When a reaction releases heat (negative ΔH) or increases the entropy of the system, these factors make ΔG more negative. On the other hand, when a reaction absorbs heat or decreases the entropy of the system, these factors make ΔG more positive.

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
$\Delta S < 0$	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)

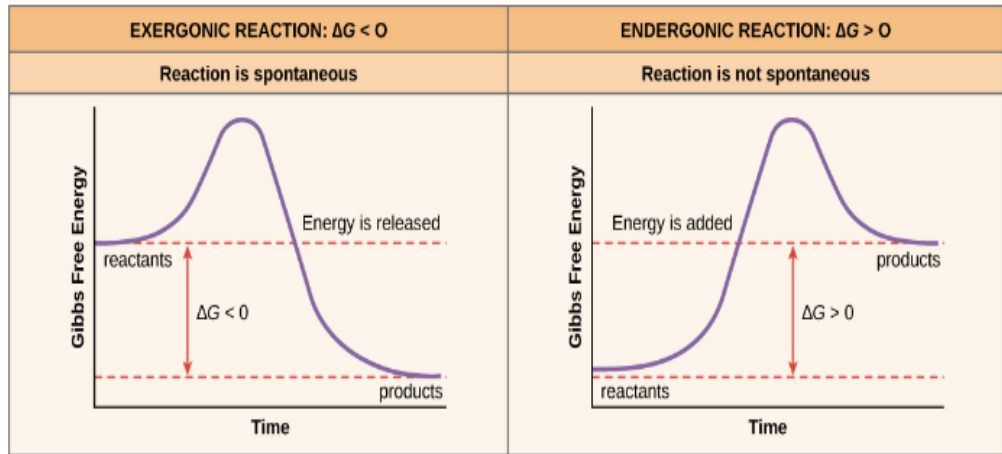
By looking at ΔH and ΔS , we can tell whether a reaction will be spontaneous, non-spontaneous, or spontaneous only at certain temperatures. If a reaction both releases heat and increases entropy, it will always be spontaneous (have a negative ΔG), regardless of temperature. Similarly, a reaction that both absorbs heat and decreases entropy will be non-spontaneous (positive ΔG) at all temperatures. Some reactions, however, have a mix of favorable and unfavorable properties (releasing heat but decreasing entropy, or absorbing heat but increasing entropy). The ΔG and spontaneity of these reactions will depend on temperature, as summarized in the table at right.

Endergonic and exergonic reactions

Reactions that have a negative ΔG release free energy and are called exergonic reactions. (Handy mnemonic: exergonic means energy is exiting the system.) A negative ΔG means that the reactants, or initial state, have more free energy than the products, or final state. Exergonic reactions are also called spontaneous reactions, because they can occur without the addition of energy.

Reactions with a positive ΔG ($\Delta G > 0$), on the other hand, require an input of energy and are called endergonic reactions. In this case, the products, or final state, have more free energy than the reactants, or initial state. Endergonic reactions are non-spontaneous, meaning that energy must be added before they can proceed. You can think of endergonic reactions as storing some of the added energy in the higher-energy products they form¹.

It's important to realize that the word spontaneous has a very specific meaning here: it means a reaction will take place without added energy, but it doesn't say anything about how quickly the reaction will happen². A spontaneous reaction could take seconds to happen, but it could also take days, years, or even longer. The rate of a reaction depends on the path it takes between starting and final states (the purple lines on the diagrams below), while spontaneity is only dependent on the starting and final states themselves. We'll explore reaction rates further when we look at activation energy.



Differences between exergonic and endergonic reaction

Exergonic Reaction	Endergonic Reaction
Chemical products have less free energy than the reactant molecules.	Products store more free energy than reactants.
Reaction is energetically downhill	Reaction is energetically uphill.
Spontaneous reaction.	Non-spontaneous reaction (requires energy input).
ΔG is negative.	ΔG is positive.
$-\Delta G$ is the maximum amount of work the reaction can perform	$+\Delta G$ is the minimum amount of work required to drive the reaction.

Energy coupling reaction

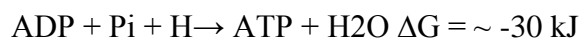
Reaction Coupling reaction in which the released energy drives an endergonic reaction

“Most biochemical pathways involve coupled reactions. In cells, an exergonic reaction is coupled to an endergonic reaction to give it free energy to drive the reaction”.

Example:

Exergonic (spontaneous) reaction

ATP Hydrolysis reaction:



Endergonic (nonspontaneous) reaction

Phosphorylation of Glucose reaction:



Coupled Reaction (showing just the key reactants & products):



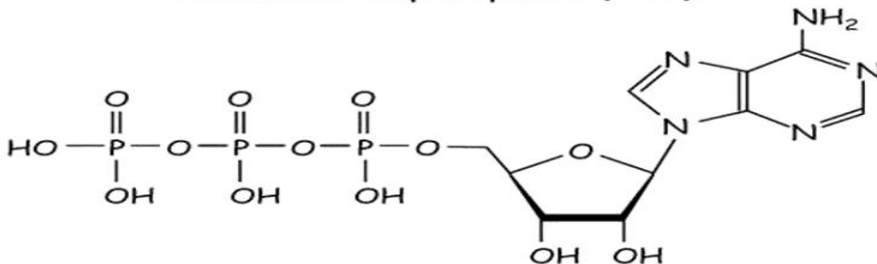
High energy compounds and energy rich bond (~):

Any bond, which on hydrolysis gives a minimum free energy of 7.4 Kcal/mol, is known as energy rich bond and the compound which has an energy rich bond is known as high energy compound. Ex. ATP, pyrophosphate, 1, 3-diphosphoglyceric acid, phosphoenol pyruvate, creatine phosphate and acetyl-CoA.

Adenosine triphosphate (ATP):

ATP is also known as the 'energy currency' of the living cell, because it transfers energy from energy yielding sources to the energy requiring cell processes. ATP has two pyrophosphate bonds. On hydrolysis of each of the terminal two phosphate groups there is release of more than 7.4 Kcal/mol of energy but the third bond yields only 3 Kcal/mol of energy, hence it is not a high energy bond. On hydrolysis ATP is converted to ADP and to AMP.

Adenosine triphosphate (ATP)



Electron transport chain(ETC)

Transfer of electrons from substrate to molecular oxygen through a chain of electron carriers is called electron transport chain or respiratory chain. Mitochondria contains a series of catalysts forming the respiratory chain which are involved in the transfer of electrons and hydrogen and their final reaction is with oxygen to form water. The components of respiratory chain are arranged sequentially in the order of increasing redox potential.

Electrons flow through the chain in a stepwise manner from lower redox potential to higher redox potential. Some amount of energy is liberated with transfer of electron from one component to another. Whenever there is a release of 7.4 Kcal of energy or a little more, then ATP formation takes place there. NADH forms 3 ATPs whereas FADH₂ forms only 2 as it enters ETC at the site beyond the first site of ATP formation.

The/three sites of ATP formation in the ETC or respiratory chain are:

1. Between NADH dehydrogenase (flavoprotein) and ubiquinone (coenzyme Q).
2. Between cytochrome-b and cytochrome-c1.
3. Between cytochrome-a and cytochrome-a₃ (cytochromes oxidase).

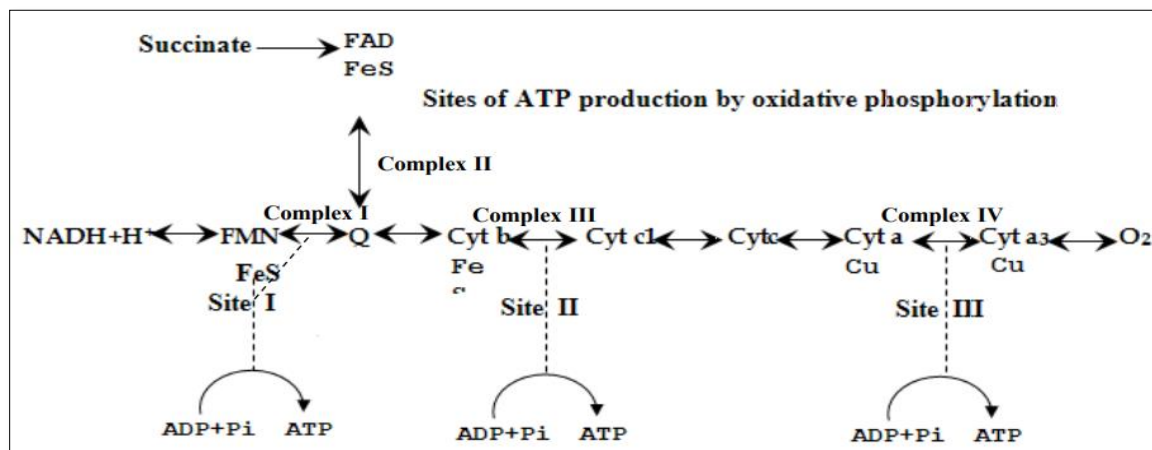


Figure: The components of ETC, their redox potential and their sequence is

Phosphorylation:

Esterification of a phosphate through a high energy bond (7.4 Kcal) is known as phosphorylation. Combination of inorganic phosphate (Pi) with any other compound through high energy bond is known as phosphorylation. Or formation of ATP from ADP and phosphate or NTP from NDP and Pi is known as phosphorylation.

P/O ratio

It is ratio of the number of molecules of ADP converted to ATP to the number of oxygen atoms utilized by respiratory chain. • It is a measure to the efficiency of oxidative phosphorylation. • It is 3/1 if NADH+H⁺ is used and 2/1 if FADH₂ is used.

There are two types of phosphorylation:

1. Substrate level phosphorylation:

Formation of high energy phosphate bond at the level of a substrate without the involvement of the respiratory chain is known as substrate level phosphorylation. Ex. Phosphoenolpyruvate is converted to pyruvate by pyruvate kinase where ATP is formed from ADP.

2. Oxidative phosphorylation:

The enzymatic phosphorylation of ADP to ATP coupled with electron transport from a substrate to molecular oxygen is known as oxidative phosphorylation or respiratory chain phosphorylation.

Mechanism of oxidative phosphorylation

Mechanism of oxidative phosphorylation was explained by three theories out of which only two theories are mentioned

There are 2 theories: 1.The chemical theory.

2.The chemiosmotic theory.

1. Chemical theory:It suggests that there is a direct chemical coupling of oxidation and phosphorylation through high-energy intermediate compounds. •This theory is not accepted, as postulated high-energy intermediate compounds were never found.

2. Chemiosmotic theory

It suggest that the transfer of electrons through the electrons transport chain causes protons to be translocated (pumped out) from the mitochondrial matrix to the intermembrane space at the three sites of ATP production (i.e. it acts as a proton pump) resulting in an electrochemical potential difference across the inner mitochondrial membrane.

Salient features of Chemiosmotic theory

- The electrical potential difference is due to accumulation of the positively charged hydrogen ions outside the membrane.
- The chemical potential difference is due to the difference in pH, being more acidic outside the membrane.
- This difference forces ATP synthase to generate ATP from ADP and inorganic phosphate.
