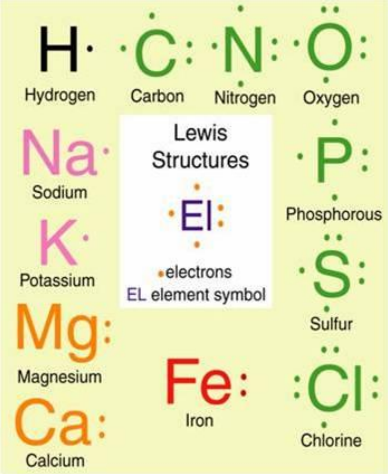
Oxidation-Reduction Reactions

Energy metabolism in all living organisms is highly dependent on metabolism providing a coordinated and regulated release of electrons from macronutrients, and their eventual use in cellular processes that regenerate ATP. Remember, electrons surround the atom of each element, and the number of electrons in a given element is dependent on the number of protons in the nucleus of the atom. For all elements of biological chemical reactivity, the electrons in the outer shell, called valence electrons, are able to be shared with other elements, forming covalent bonds. The valence electrons of specific elements are presented as Lewis Structures. Also remember that chemical reactions are constrained by the 'Rule of 8s" in that biological active elements can react with other elements so that a maximum of 8 electrons are in the collective outer shell. For example, Carbon can gain 4 added electrons, Nitrogen 3, Oxygen 2, Phosphorous 3, Sulfur 2 and Chlorine 1. During these chemical reactions, some of these electrons are removed and added to other elements involved in the reaction to change the structure of chemical compounds. Hence, understanding chemical reactions also means understanding the movement of electrons at the element and compound levels. This is why the study of chemistry is essential for all students of exercise physiology!



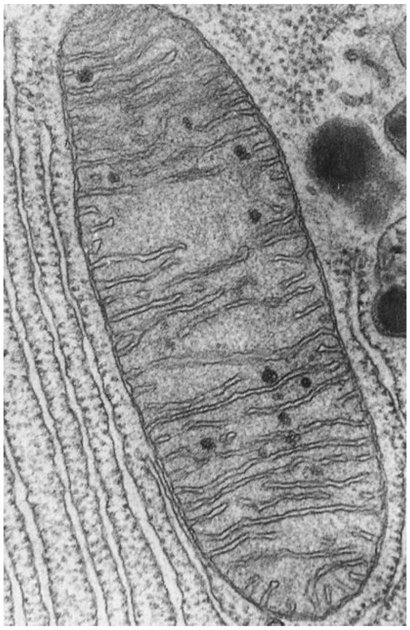


Figure 1. An electron micrograph of a typical mitochondrion. Notice the two membranes, as well as the inner folds if the internal membrane forming cristae.

Let's start in the beginning. Food is our source of electrons, as well as chemical energy and certain micronutrients essential for life and health. Often times the macronutrient energy and micronutrient benefits of food ingestion dominate how nutrition and biochemistry is taught. However, be aware that within the "energy" benefit of food ingestion is also the vital importance of electron transfer. The organelle within cells that directs such electron flow to ATP regeneration is the mitochondrion (Figures 1 and 2). However, for the mitochondria to use electrons, they must first be removed from molecules. This is the role of oxidation-reduction reactions, and these occur both within and outside (in cytosol) of mitochondria.

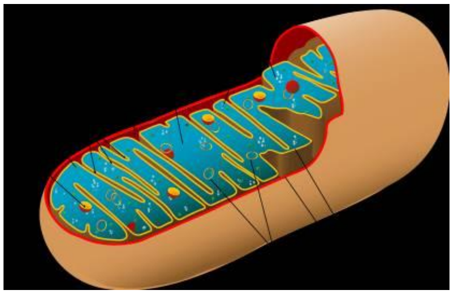


Figure 2. A diagram of a mitochondrion.

Oxidation-Reduction Reactions

Oxidation is defined as the removal or loss of electrons. Thus, a molecule that loses electrons becomes **oxidized**. These removed electrons have to go somewhere, and in an oxidation reaction, they are transferred to another of the substrates. The substrate that receives or gains the electrons becomes **reduced**. Thus, **reduction** involves the gaining of electrons. Therefore, oxidation and reduction occur hand-in-hand, and hence the term **oxidation-reduction**. The substrate giving the electrons is called the **oxidant**, and the substrate receiving the electrons is the **reductant**. Obviously, the oxidized and reduced molecules are now the products of the reaction. As you have already learned, enzymes that catalyze oxidation-reduction reactions typically have trial names ending in the word "dehydrogenase".

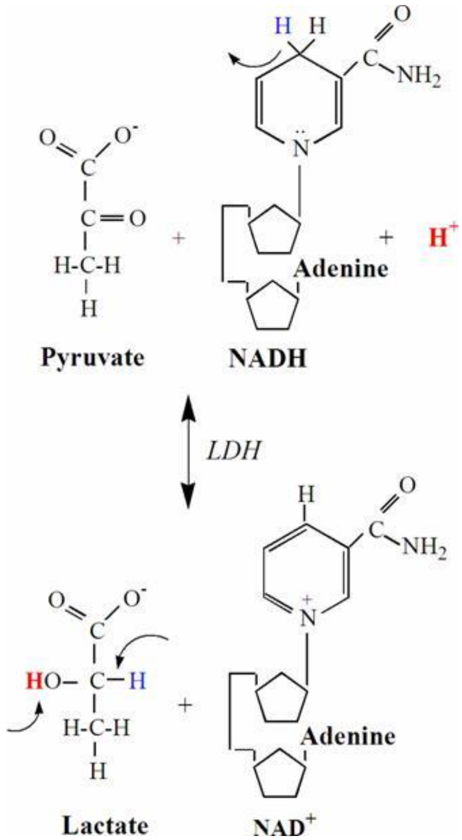


Figure 3. The lactate dehydrogenase reaction is an example of an oxidation-reduction reaction within energy catabolism.

Many of the reactions of glycolysis, which you will soon study, are oxidation-reduction reactions. We will look at a couple of these soon. First of all, make sure you have read and understand the basic chemistry within the Topic "Atoms, Electrons, Charge and Chemical Reactions".

A great example of an oxidation-reduction reaction is the lactate dehydrogenase reaction (Figure 3). Based on Figure 3, try to determine which substrate is the oxidant and which is the reductant. The hint for this is to look at the complexity of the structures. Compare the structure of lactate to pyruvate, and the structure of NAD^+ to NADH. The metabolites that are the more complex, or that have more bonds and hydrogens, have more electrons. It has to be this way, as the only way to have more of the same elements is to have more electrons as these are required to be shared to form the added covalent bonds! Thus, pyruvate is reduced to lactate, and NADH is oxidized to NAD^+.

Often, but not always, hydrogen ions (H^+) are involved in the oxidation-reduction as well. This is seen in Figure 3 for the reduction of NAD^+ to NADH. Pyruvate is reduced by 2 electrons (from NADH) and gains 2 H^+ (1 from NADH and 1 from solution) to form lactate. Note that the hydrogen ion (H^+) is a hydrogen atom that has lost its only electron, causing it to have a single positive charge; hence the H^+ abbreviation. You will later learn of the importance of the H^+ to pH and the development of metabolic acidosis.

Cellular energy metabolism involves several **electron carriers**. Both **nicotinamide adenine dinucleotide (NADH:NAD^+)** (derived from **niacin**) (Figure 4) and **flavin**

Oxidation-Reduction Reactions

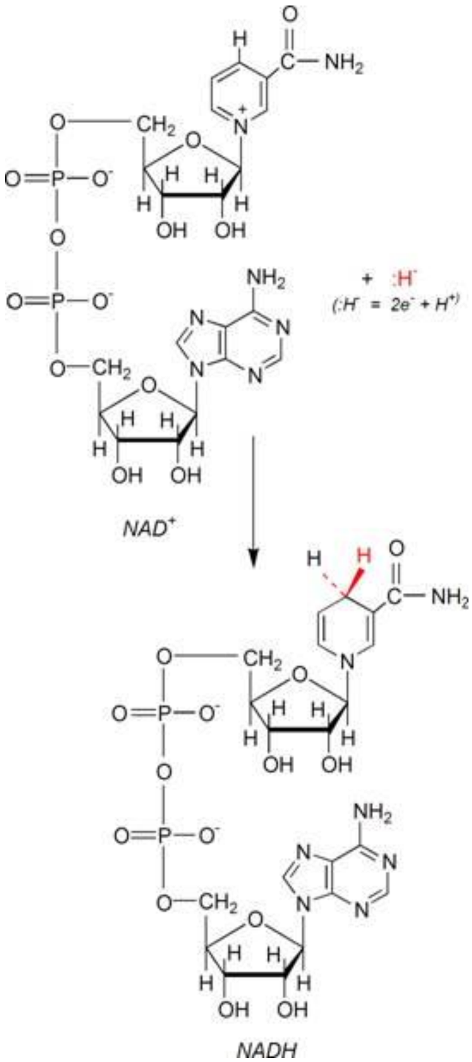


Figure 4. The chemical structure of NAD$^+$ and NADH.

adenine dinucleotide ($FADH_2$:FAD^+) (derived from vitamin B2 = **riboflavin**) (Figure 6) are involved in the capture and transfer of electrons during the catabolism of carbohydrates and fats. **Nicotinamide adenine dinucleotide phosphate (NADPH)** (Figure 5) provides the electrons for the oxidation-reduction reactions of anabolism. The **flavoprotein** component **flavin monoucleotide (FMN)** of $FADH_2$ is also involved in electron transfer within the **electron transport chain** located within and along the inner mitochondrial membrane.

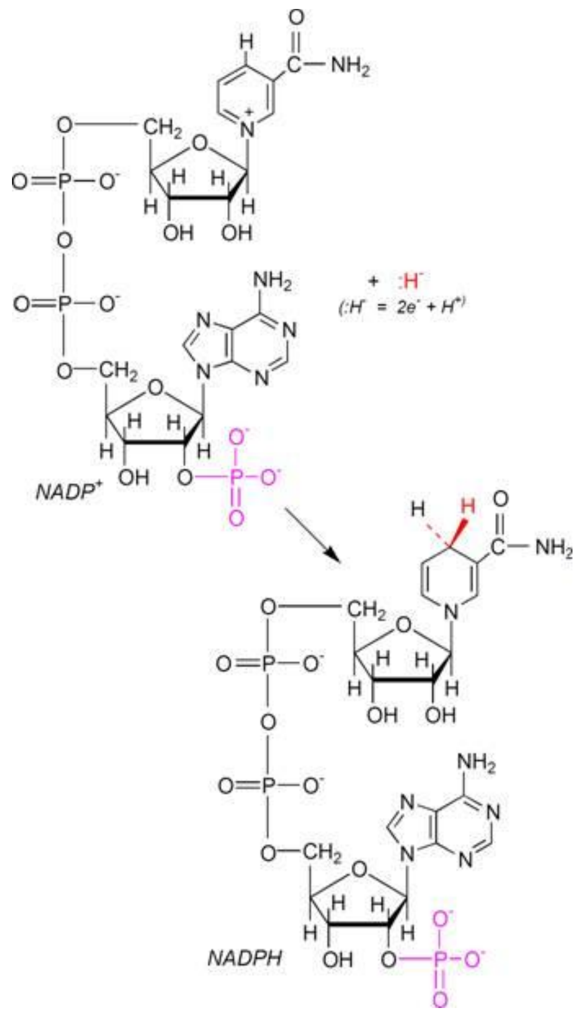


Figure 5. The chemical structure of NADP$^+$ and NADPH.

Oxidation-Reduction Reactions

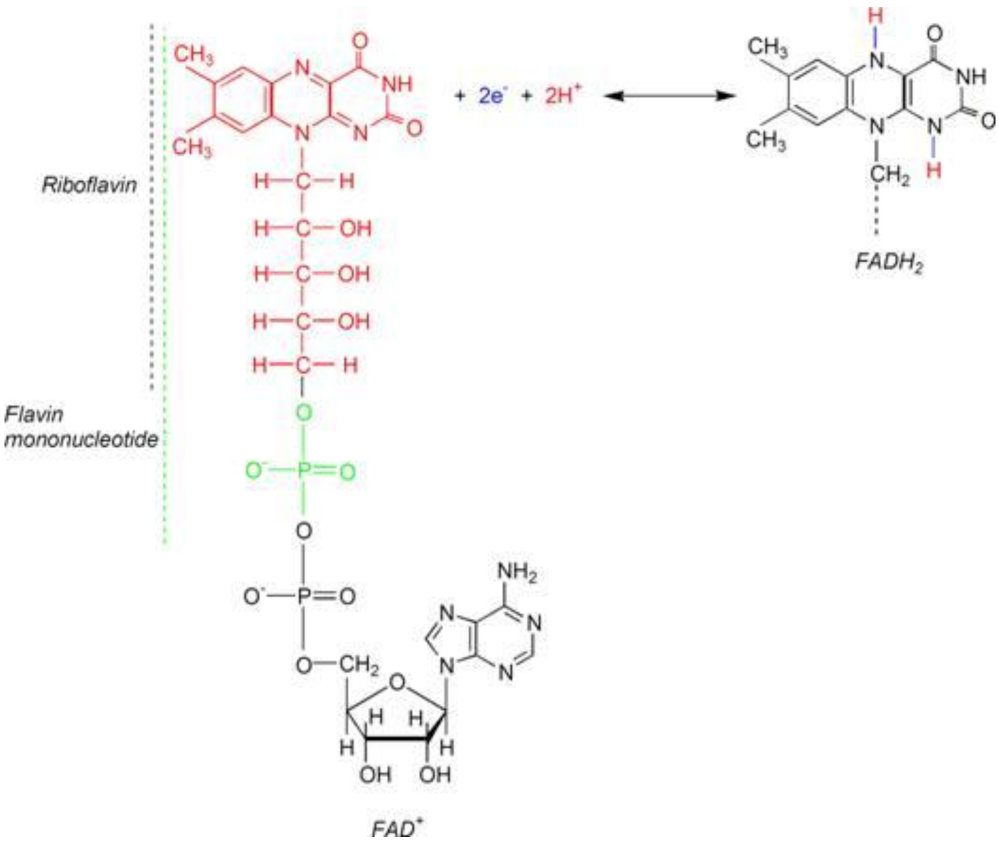


Figure 6. The chemical structure of FAD and $FADH_2$. Note the subcomponent of FAD called flavin mononucleotide (FMN).

Glossary Words

oxidation involves the removal or loss of electrons.

oxidized refers to the process where a molecule has lost one or more electrons.

reduced refers to the process where a molecule has gained one or more electrons.

reduction refers to the gaining of electrons.

oxidation-reduction is the ombined term to describe a reaction where one substrate is oxidized and the other is reduced.

oxidant is the substrate that was oxidized (gave up electrons).

reductant is the substrate that was reduced (gained electrons).

Oxidation-Reduction Reactions

electron carriers are molecules that assist electron and proton transfer through the cell.

nicotinamide adenine dinucleotide ($NADH:NAD^+$) is the electron carrier derived from niacin where NAD^+ is the oxidized form.

niacin is the B group vitamin source of the main structural component of $NADH:NAD^+$.

flavin adenine dinucleotide ($FADH_2:FAD^+$) is the electron carrier derived from riboflavin where FAD^+ is the oxidized form.

riboflavin is the B-group vitamin source of the main structural component of $FADH_2:FAD^+$.

nicotinamide adenine dinucleotide phosphate (NADPH) is the electron carrier derived from niacin which is predominantly operative in anabolism, where $NADP^+$ is the oxidized form.

flavoprotein is an enzyme that catalyzes oxidation-reduction reactions using either FAD^+ or flavin mononlucleotide (FMN) as electron carriers.

flavin monoucleotide (FMN) is a flavin derived electron acceptor involved in the electron transport chain of the mitochondria.

electron transport chain is the pathway within mitochondria, located within the inner mitochondrial membrane, where electrons (and protons) are exchanged from electron carriers within the mitochondrial matrix to electron and proton receivers along the chain.