

Energy, Enzymes & Biological Reactions

Biogenetics:

Principles of thermodynamics applied to reactions and process of cells. Allows insight into how cells handle energy transactions.

System + Surroundings:

Closed: no energy exchange Open: energy can be added or removed Every change produces either heat or work

For Thermodynamic Measurements:

Standard conditions pH=7, T=25 degrees C, 1 Atm, Pressure State usually constant under biological conditions

First law of thermodynamics:

Energy cannot be created or destroyed, but it can be changed from one form to another.

Second law of thermodynamics:

Whenever changes form, entropy increases. Whenever energy changes form, some energy is lost (unusable by the organism. Energy is conserved as a whole, but not in any system doing work.

Metabolism:

the sum of all chemical reactions in an organism a **balance** between reactions which release energy and those that require energy

Catabolism:

food molecules broken down to release energy

Anabolism:

complex organic molecules synthesized from simpler ones- energy input is needed

Enzymes:

Guide metabolic pathways

Energy, Enzymes & Biological Reactions (cont)

Gibb's Free Energy:

Energy released that is available to do useful work

Spontaneous

processes occur without energy input, and increase entropy.

Non-spontaneous:

processes require energy input

Biological Order & Disorder

Energy flows into ecosystems as sunlight and exits as

heat

Living organisms

Convert sunlight to chemical energy. Use this chemical energy to do work. Generate heat and disorder on the process (increases entropy)

Entropy

may decrease in living things (living things show order), but the total entropy of the universe increases in the process

Life

uses energy to create order but thus energy also creates disorder.

Free- Energy Change, ΔG

Gibbs Free energy G

the energy in a system that can do work. The change in free energy (ΔG) during a reaction.

Whether the reaction will be

Spontaneous and release energy (exergonic) or be **Non spontaneous** and store energy (endergonic)

$\Delta G =$

$\Delta H - T\Delta S$

Free- Energy Change, ΔG (cont)

ΔH

is the change in total energy (enthalpy)

ΔS

is the change in entropy

T

is the temperature in kelvin ($K = C + 273.15$)

$\Delta G =$

the reaction is spontaneous, exergonic, and provides energy for work.

Enzymes

speed up reactions, but don't change ΔG

Mitochondria and ATP

Animals, plants, fungi, and most protists depend on mitochondria for energy to grow and survive.

ATP forms in mitochondria as stored chemical energy available to do cellular work

harvested from energy released in reactions that break down food molecules.

Cellular Respiration

Collection of metabolic reactions that breakdown food molecules and stores energy as ATP

Aerobic and Anaerobic respiration

Aerobic respiration:	Form of cellular respiration in eukaryotes and many prokaryotes	Oxygen is needed in the ATP producing process
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Aerobic and Anaerobic respiration (cont)

Anaerobic respiration: Form of cellular respiration in some prokaryotes. A molecule other than oxygen, such as sulfate or nitrate, is used in the ATP producing process.

Oxidation

The removal of electrons from a substance. The substance from which the electrons are removed (The electron donor) is **oxidized**.

Stored Energy is released

Reduction

The addition of electrons to a substrate. The substrate that receives the electron (the electron acceptor) is **reduced**.

Energy is stored

Redox Reactions

Oxidation and reduction reactions always coupled **Redox Reactions**.

Reactions that move electrons from a donor molecule and simultaneously add them to an acceptor molecule.

Summary: Cellular Respiration

Cellular respiration includes reactions that transfer electrons from organic molecules (such as glucose) to oxygen, and reactions that make ATP.

C

6H

Electrons carriers such as NAD+

move electrons from fuel molecule to cellular destinations

1st stage of Glycolysis

Enzymes break a 6-carbon molecule of glucose into two 3 carbon molecules of pyruvate.

Some ATP is synthesized by **substrate-level phosphorylation**, an enzyme catalyzed reaction that transfers a phosphate group from a substrate to ADP.

Some electrons are carried away by NADH.

2nd stage of Pyruvate oxidation

Enzymes convert the 3-carbon pyruvate into a 2-carbon acetyl group, which enters the **citric acid cycle** and is completely oxidized to carbon dioxide.

Some ATP is synthesized during the citric acid cycle.

Lots of reduced electron carriers carry away electrons as NADH and FADH.

3rd Stage Oxidative Phosphorylation

High energy electrons are delivered to oxygen by a sequence of reduced electron carriers in the **electron transport chain**.

Free energy released by electron flow generates an H⁺ gradient by **chemiosmosis**.

ATP synthase uses the H⁺ gradient as the energy source to make ATP.

Substrate level Phosphorylation

Occurs when enough energy is released in a reaction step to pass phosphate onto ADP.

Glycolysis: Splitting Sugar in half

Glycolysis (Embden-Meyerhof pathway) breaks 6-carbon glucose into two molecules of 3 carbon pyruvate in 10 sequential enzyme catalyzed reactions.

Glycolysis takes place in the cytosol of all organisms.

Energy flow in glycolysis

The initial steps of glycolysis require energy. 2 ATP are hydrolyzed.

4 ATP are produced by substrate-level phosphorylation for a net gain of 2 ATP.

The electron carrier NAD⁺ is reduced to NADH, which carries 2 electrons and a proton (H⁺) removed from fuel molecules.

Pyruvate Oxidation and the Citric Acid Cycle

Active transport moves pyruvate into mitochondria matrix where pyruvate oxidation and the citric acid cycle take place.

Oxidation of pyruvate generates CO₂, **acetyl-coenzyme A (acetyl-CoA)**, and NADH.

The acetyl group of acetyl-CoA enters the citric acid cycle.

Overview of citric acid cycle

Citric acid cycle, carbon products of pyruvate oxidation are oxidized to CO₂.

All viable electrons are transferred to 3NAD⁺ (NADH) and 1FAD (FADH).

Each turn of the citric acid cycle produces 1 ATP by substrate-level phosphorylation.

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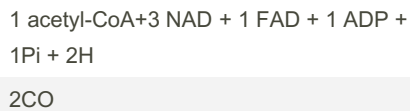
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Summary: The citric acid cycle

The eight reactions of the **citric acid cycle (tricarboxylic acid cycle, or krebs cycle)** oxidize acetyl groups completely to CO generate 3 NADH and 1 FADH and synthesize 1 ATP by substrate level phosphorylation



Oxidative Phosphorylation ETS & Chemiosmosis

High energy electron removed from fuel molecules and picked up by carrier molecules-are released into the electron transfer system of mitochondria

Mitochondrial electron transfer system (ETS)

Series of electron carriers that alternately pick up and release electrons and ultimately transfer them to their final acceptor-oxygen

Electron Flow

Individual electron carriers of the ETS are organized specifically from high to low free energy

NADH and FADH contain the most free energy and are easily oxidized

The terminal electron acceptor (O₂) is most easily reduced

Electron movement through the system is spontaneous, releasing free energy

Electron Transfer System from high to low free energy

Energy Flow in the ETS

In the ETS electrons release free energy used to build the H gradient across the inner mitochondrial membrane

High H concentration in the inter membrane compartment

Low H concentration in the matrix

The H gradient supplies energy that drives ATP synthesis by mitochondria ATP synthase

Transfers Between Proteins

Two small, mobile electron carriers, cytochrome C and ubiquinone (coenzyme Q) shuttle electrons between the major complexes

Cytochromes

Proteins with a heme prosthetic group that contains an iron atom that accepts and donates electrons

Forming the H Gradient

Ubiquinone and complexes I, III, and IV actively transport protons (H⁺) from matrix to inter membrane compartment

Concentration of H in the inter membrane compartment generates an electrical and chemical gradient across the inner mitochondrial membrane

Proton-motive force

Stored energy produced by proton and voltage gradient

Energy is used for ATP synthesis and cotransport of substances to and from mitochondria

ATP Synthase and Chemiosmosis

In the mitochondrion, ATP is synthesized by ATP synthase, an enzyme embedded in the inner mitochondrial membrane

The H gradient powers ATP synthesis by ATP synthase by **chemiosmosis**

ATP synthase uses proton-motive force to add phosphate to ADP to generate ATP (phosphorylation)

ATP synthase structure and function

A basal unit in the inner membrane is connected by a stalk to a headpiece located in the matrix- a peripheral stator bridges the basal unit and headpiece

Proton-motive force moves protons in the inter membrane space through the enzyme's basal unit into the matrix

H flow powers ATP synthesis by rotation of the ATP synthase headpiece (chemiosmosis)

Conservation of chemical Energy

Hydrolysis of ATP to ADP yields about 7.0 kcal/mol-total energy conserved in 32 ATP is about 224 kcal/mol

Glucose burned in the air releases 686 kcal/mol

Efficiency of cellular glucose oxidation $(224/686 \times 100) = 33\%$

The rest of the chemical energy is released as body heat

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Fermentation can re-oxidize NADH

When oxygen is absent or limited, electrons carried by the 2 NADH produced by glycolysis may be used in fermentation

Otherwise, glycolysis will stop due to lack of NAD

Recall: NAD accepts electrons in reaction 6 of glycolysis

Fermentation

Electrons carried by NADH are transferred to an organic acceptor molecule (convert NADH to NAD)

Glycolysis continues to supply ATP by substrate level phosphorylation

Lactate fermentation

Converts pyruvate into lactate

Occurs in some bacteria, plant tissues, skeletal muscle

Used to make buttermilk, yogurt, dill pickles

Alcoholic fermentation

Converts pyruvate into ethyl alcohol and CO₂

Occurs in some plant tissues, invertebrates, protists, bacteria, and single-celled fungi such as yeasts

Used to make bread and alcoholic beverages

Interrelationships of Catabolic Anabolic Pathways

Many carbohydrates, lipids, and proteins can be hydrolyzed and their products are directed into various stages of cellular respiration to be oxidized as fuel

CoA directs products of many oxidative pathways into the citric acid cycle

Oxidation of Fats

Oxidation of fats produces more than twice the energy of oxidation of proteins or carbohydrates

Before entering oxidative reactions, triglycerides are hydrolyzed into glycerol and individual fatty acids

Oxidation of proteins

The amino group is removed

The remainder enters oxidative pathways as pyruvate, acetyl-CoA, or intermediates of the citric acid cycle

Many Pathways Start Glycolysis or the Citric Acid

Glycolysis and the citric acid also supply molecules from which many other cellular molecules are synthesized

Additionally, when energy is not needed by the body, glucose can be synthesized from intermediates of these pathways in the process of **gluconeogenesis**

Gluconeogenesis: which consumes ATP rather than producing it

Glycolysis and Citric acid Cycle Regulation

ATP and NADH production are balanced against glucose conservation by systems that regulate enzymes of glycolysis and the citric acid cycle

If excess ATP is present in cytosol, ATP binds to phosphofructokinase (in reaction 3) slowing or stopping enzyme action by feedback inhibition in order to regulate glycolysis

If excess ATP or citrate is present in the mitochondria, one of these binds to citrate synthase, slowing or stopping enzyme action by feedback inhibition in order to regulate the citric acid cycle