8 Metabolism, cell respiration and photosynthesis

Introduction
- life sustained by web of chemical reactions in cells: regulated by needs of cell and organism
- energy converted to usable form in cell respiration; photosynthesis converts light energy to chemical energy and huge diversity of carbon compounds is produced

8.1 Metabolism

Metabolic pathways
- consist of chains and cycles of enzyme-catalyzed reactions
- metabolism refers to chemical changes taking place in living cell
- metabolism is very complex, but there are some common patterns: chemical changes happen in sequence of small steps (metabolic pathway), metabolic pathways involve a chain of reactions, some metabolic pathways form a cycle (end product is also reactant starting it)

Enzymes and activation energy
- enzymes lower activation energy of chemical reaction they catalyze
- chemical reactions are not single-step processes: substrates pass through transition state
- energy is required to reach transition state (activation energy); though from transition state to product energy is released
- activation energy is used to break or weaken bonds
- enzyme catalyzing reaction: substrate binds to active site, enzyme alters substrate to reach transition state, converted into products, separate from active site
- binding to active site lowers overall energy level of transition state: activation energy reduced
- net amount of energy released stays unchanged by enzyme's involvement
- reduced activation energy greatly increases rate of reaction (typically by factor million+)

Types of enzyme inhibitors
- some chemical substances bind to enzymes and reduce its activity: inhibitors
- inhibitors can be competitive and non-competitive
- competitive: interfere with active site so the substrate cannot bind
- non-competitive: bind at different location than active site causing change in shape of enzyme so the substrate cannot bind

End-product inhibition
- allosteric interactions: many enzymes regulated by chemical substances binding to special sites away from active site (allosteric site)
- in many cases the regulated enzyme is one of first reactions in metabolic pathway and the substance binding to allosteric site is end product of pathway
- reactions often do not reach completion: equilibrium is reached with substrate-product ratio: if product concentration increases reaction slows and eventually stops: end-product inhibition prevents build-up of intermediate products

8.2 Cell respiration

Oxidation and reduction
- oxidation and reduction are chemical processes that always occur together; involves a transfer of electrons: oxidation is the loss of electrons, reduction is the gain of electrons
- electron carriers: substances that can accept and give up electrons as required
- main electron carrier in respiration is NAD, in photosynthesis it is NADP (phosphorylated NAD)
- NAD initially has one positive charge and exists as NAD^+
- NAD^+ accepts two electrons: two hydrogen atoms are removed from substance being reduced, one hydrogen atom is split into proton and electron, NAD^+ accepts the electron and the proton is released, NAD accepts electron and proton of other hydrogen atom creating NADH and H^+

- reduction can be achieved by accepting atoms of hydrogen; oxidation by loss of hydrogen
- oxidation and reduction can also occur through loss or gain of atoms of oxygen
- adding oxygen atoms is oxidization because oxygen atoms have a high affinity for electrons and tend to draw electrons from other molecules

Phosphorylation

- addition of a phosphate molecule (PO_4^{3-}) to an organic molecule
- purpose of phosphorylation is to make a molecule more unstable: activates the molecule
- hydrolysis of ATP releases energy: exergonic reaction; many reactions in body are endergonic
- reactions in body do not proceed unless coupled with exergonic reaction releasing more energy
- many metabolic reactions are coupled to the hydrolysis of ATP

Glycolysis and ATP

- most significant consequence of glycolysis is production of small ATP yield without oxygen
- glycolysis converts sugar into pyruvate: is not done in one step (metabolic pathway)
- first step of glycolysis: ATP is used to phosphorylate sugar: reduces activation energy: makes the reaction much more likely to occur

Pyruvate is a product of glycolysis

- fructose bisphosphate is split from two molecules of triose phosphate: each is oxidized to glycerate-3-phosphate in reaction that yields enough energy to make ATP, oxidization is made by removing hydrogen atoms, hydrogen is accepted by NAD^+ which becomes NADH and H^+
- in final stage of phosphate is transferred to ADP to produce more ATP and pyruvate

The fate of pyruvate

- two pyruvate are produced per glucose in glycolysis
- if oxygen is available, pyruvate is absorbed into mitochondrion where it is fully oxidized
- carbon and oxygen are removed as carbon dioxide in decarboxylation
- oxidation of pyruvate is achieved by removal of pairs of hydrogen atoms: NAD and FAD accept hydrogen atoms and pass them to electron transport chain for oxidative phosphorylation

The link reaction

- after pyruvate is shuttled into mitochondrial matrix, it is decarboxylated and oxidized to form an acetyl group (acetyl coenzyme A); two high energy electrons are removed and react with NAD^+ to produce reduced NAD
- whole process is link reaction as it links glycolysis with Krebs cycle

The Krebs cycle

- link reaction involves one decarboxylation and one oxidation; in Krebs cycle two decarboxylations and four oxidations follow
- energy released in oxidations of link reaction and Krebs cycle is used to reduce hydrogen carriers (NAD^+, FAD): energy is used in final part of aerobic cell respiration
- for every turn of Krebs cycle, it produces three reduced NAD, two decarboxylations occur, one reduced FAD is produced, one ATP molecule is generated

Oxidative phosphorylation

- reduced NAD is generated in glycolysis, link reaction, Krebs cycle, $FADH_2$ is produced during Krebs cycle
- final part of aerobic respiration is oxidative phosphorylation because ADP is phosphorylated to produce ATP using energy released by oxidation
- NAD and $FADH_2$ are used to carry the energy released to the mitochondrial cristae

The electron transport chain

- main substance oxidized is NAD
- energy is released in series of small steps, carried out by chain of electron carriers
- reduced NAD and $FADH_2$ donate their electrons to electron carriers
- as electrons pass from carrier to carrier, energy is used to transfer protons across inner membrane form matrix into intermembrane space

- protons flow through ATP Synthase down their concentration gradient providing energy for the production of ATP

Chemiosmosis

- mechanism used to couple release of energy by oxidization to ATP production
- happens in the inner mitochondrion membrane
- chemical substance (H^+) moves across a membrane, down the concentration gradient: releases energy needed for enzyme ATP synthase to make ATP
- main steps: NADH and H^+ supplies pair of hydrogen atoms to first carrier (NAD+ returns to matrix), hydrogen atoms are split to release two electrons, electrons pass from carrier to carrier and energy is released, energy transfers protons (H^+) across inner mitochondrial membrane, concentration gradient builds up quickly, gradient is store of potential energy, to allow electrons to flow they must be transferred to terminal electron acceptor (in aerobic respiration it is oxygen), the oxygen combines with two H^+ ions from matrix to become water, protons pass back from intermembrane space to matrix through ATP synthase, this releases energy and is used to phosphorylate ADP

The role of oxygen

- oxygen is final electron acceptor in mitochondrial electron transport chain
- reduction of oxygen molecule involves accepting electrons and forming covalent bond with H
- by using hydrogen, proton gradient is maintained so that chemiosmosis can continue

Structure and function in the mitochondrion

- clear relationship between structures in organism and their function: natural selection, evolution
- mitochondria which produced most ATP would have an advantage
- adaptation: change in structure so that something carries out its function more efficiently
- mitochondrion is semi-autonomous organelle: can grow and reproduce itself
- mitochondrion is site of aerobic respiration; outer membrane separates contents of mitochondrion from rest of cell: creates compartment specialized for biochemical reactions
- inner mitochondrial membrane is site of oxidative phosphorylation: contains electron transport chains and ATP synthase
- cristae are tubular projections which increase surface available for oxidative phosphorylation
- intermembrane space is where protons build up after electron transport chain
- volume of intermembrane space is small so concentration gradient can be built up rapidly
- matrix fluid contains enzymes necessary for Krebs cycle and link reaction

8.3 Photosynthesis

Location of light-dependent reactions

- photosynthesis consists of two different parts: one which uses light directly (light-dependent reactions) and the other that uses light indirectly (light-independent reactions)
- light-dependent reactions can only carry on in darkness for few seconds
- chloroplast has outer and inner membrane; inner membrane encloses third system of interconnected membranes: thylakoid membranes; within these is thylakoid space
- light-dependent reactions take place in thylakoid space and across thylakoid membranes

The products of the light-dependent reactions

- light energy is converted to chemical energy in the form of ATP and reduced NADP
- ATP and reduced NADP are energy sources for the light-independent reactions

The location of the light-independent reactions

- inner membrane of chloroplast encloses a compartment called stroma which is a protein-rich medium containing enzymes for light-independent reactions (Calvin cycle)
- Calvin cycle is an anabolic pathway that requires endergonic reactions to be coupled to hydrolysis of ATP and oxidation of reduced NADP

Photoactivation

- Chlorophyll and accessory pigments are grouped into large arrays called photosystems

- photosystems are located in the thylakoids; there are two types: Photosystems I and II
- photosystems have reaction centers
- both photosystems contain many chlorophyll molecules, which absorb light energy and pass it to two special chlorophyll molecules in the reaction centre of the photosystems
- when the special chlorophyll molecules absorb energy from a photon of light, an electron within the molecule becomes excited: the chlorophyll is photoactivated
- chlorophyll at reaction centre can donate their excited electrons to an electron acceptor
- light-dependent reactions begin in Photosystem II; electron acceptor in this photosystem is called plastoquonine: collects two excited electrons from Photosystem II and moves to another position in membrane
- plastoquonine is hydrophobic so it remains within the membrane
- absorption of two photons of light causes production of one reduced plastoquonine with one of chlorophyll at reaction centre having lost two electrons
- Photosystem II can do this twice so chlorophyll at reaction centre loses four electrons and two plastoquonine molecules have been reduced

Photolysis

- when plastoquonine is reduced, chlorophyll in reaction centre is a powerful oxidizing agent: causes water molecules to split (photolysis) and give up electrons, replacing the ones it lost
- photolysis is how oxygen is generated and diffuses away as a waste product
- useful product of Photosystem II is reduced plastoquonine, carrying electrons and light energy
- the light energy drives all the subsequent reactions of photosynthesis

The electron transport chain

- photophosphorylation: production of ATP using energy from light, carried out by thylakoids
- thylakoids are stacks of membranes with very small fluid-filled spaces; contain Photosystem II, ATP synthase, chain of electron carriers, Photosystem I
- plastoquonine carries electrons to start chain of electron carriers

The proton gradient

- electrons are passed from carrier to carrier in the electron transport chain
- energy is released as they pass which pumps protons across thylakoid membranes into space inside the thylakoids
- concentration gradient of protons develops which stores potential energy; photolysis contributes to this gradient

Chemiosmosis

- protons travel back across membrane, down concentration gradient, through enzyme ATP synthase: energy released is used for making ATP from ADP and inorganic phosphate
- when electrons reach end of carrier chain they are passed to plastocyanin
- plastocyanin: water-soluble electron acceptor in fluid in thylakoids
- reduced plastocyanin is used in the next step of photosynthesis

Reduction of NADP

- remaining parts of light-dependent reactions involve Photosystem I: reduced NADP is important product: needed in light-independent reactions; carries a pair of electrons
- chlorophyll in Photosystem I passes light energy to special chlorophyll molecules in reaction centre: raises electron to high energy level: photoactivation
- excited electron passes through carrier chain and is passed at the end to ferredoxin
- ferredoxin is a protein in fluid outside of thylakoid
- two molecules of reduced ferredoxin are used to reduce NADP
- electron lost from Photosystem I to carrier chain is replaced by electron from plastocyanin
- Photosystem II and I are linked: excited electrons from Photosystem II are passed through chain of carriers to plastocyanin which gives them to Photosystem I, electrons are re-excited with light energy and are used to reduce NADP
- when NADP runs out, electrons return to electron transport chain that links the photosystems: as electrons flow back along electron transport chain to Photosystem I, they cause pumping of protons which allows ATP production: cyclic photophosphorylation

Carbon fixation

- carbon fixation reaction: carbon dioxide is converted into other carbon compounds
- in plants and algae this happens in stroma (fluid surrounding thylakoids in chloroplast)
- product of reaction is glycerate-3-phosphate
- carbon dioxide reacts with five-carbon compound (ribulose bisphosphate, RuBP) to produce two molecules of glycerate-3-phosphate
- enzyme catalyzing reaction is ribulose bisphosphate carboxylase (rubisco)
- stroma contains large amounts of rubisco to maximize carbon fixation

The role of reduced NADP and ATP in the Calvin cycle

- RuBP is 5-carbon sugar derivative; when it is converted to glycerate-3-phosphate amount of hydrogen in relation to oxygen is reduced
- hydrogen has to be added using ATP and reduced NADP (from light-dependent reactions) by reduction reaction to produce carbohydrate
- ATP provides energy and reduced NADP provides hydrogen atoms
- product is a three-carbon sugar derivative: triose phosphate

The fate of triose phosphate

- first carbohydrate produced by light-independent reactions is triose phosphate
- two triose phosphate molecules can be combined to hexose phosphate; hexose phosphate can be combined by condensation reaction to starch
- if all triose phosphate was converted, supplies of RuBP would run out
- some triose phosphate in chloroplast is used to regenerate RuBP; conversion of 3-carbon sugar into 5-carbon sugar cannot be done in one step
- RuBP is consumed and produced in light-independent reactions: Calvin cycle
- three RuBP form six triose phosphates: five of these are needed to regenerate three RuBP molecules: only one triose phosphate is left for conversion to hexose, starch, other products
- to produce glucose, six turns of Calvin cycle are needed, each of which contributes one of the fixed carbon atoms

RuBP regeneration

- in last phase of Calvin cycle, series of enzyme-catalyzed reactions convert triose phosphate to RuBP using ATP
- after RuBP is regenerated it can serve to fix carbon dioxide and begin cycle again

Chloroplast structure and function

- double membrane forms chloroplast envelope
- thylakoids: extensive system of internal membranes, intense green color
- small fluid-filled samples inside thylakoids
- stroma: colorless fluid around thylakoids containing many different enzymes; may contain starch grains or lipid droplets if chloroplasts synthesize rapidly
- grana: stacks of thylakoids