Enzymes

Free energy; $\Delta G = \Delta H - T\Delta S$; Spontaneous vs. non-spontaneous reactions
LeChatelier's Laws of equilibrium
Energy of Activation (E_a) determines the rates of chemical reactions; enzymes affect E_a
Lock-and-Key theory of enzyme-substrate interaction; Induced-fit model of binding
Michaelis-Menton Model of Enzyme Catalysis; M&M Equation
Lineweaver-Burke (linear) form of M&M Equation
Turnover number: $V_{max} = k_3 [E]_t$ or $k_3 = V_{max}/[E]_t$
Km is equal to the dissociation constant; K_m is proportional to 1/substrate affinity
Inhibition: Irreversible: heavy metals, covalent bonding, etc.
Inhibition: competitive and non-competitive
Infinite substrate concentration overcomes competitive inhibition.
Recognize both types of competition on M&M and Linewaver-Burke plots
Penicillin: contains β-lactam ring; inhibitor of transpeptidase enzyme.
Other "-cillins" also function in similar fashion, some with enhanced acid resistance.
Sulfa drugs are competitive inhibitors of enzymatic conversion of PABA in bacteria.

Enzyme Mechanisms

Lysozyme
Carbonic anhydrase
Zymogens: trypsin, chymotrypsin, elastase, prothrombin, etc.
Zymogens all contain electron-transfer network;
Protection from zymogens:
they are synthesized in inactive forms called zymogens;
they are stored in crystalline granules;
powerful trypsin inhibitor is bound to enzyme in pancreas
Blood clotting is accomplished by a cascade of zymogen activations
Interactions of Factor X, thrombin, fibrin, clot
Role of vitamin K in processing prothrombin; formation of γ-carboxyglutamates
Vitamin K antagonists: dicoumarol and warfarin

Carbohydrates

Empirical formula: $C \bullet H_2O$; 6-carbon sugars have molecular formulas of $C_6H_{12}O_6$,
Ribose is a 5-carbon aldose, C_5H_{10},O_5
Sugars are classified as aldoses or ketoses; these forms can often isomerize from one to another
Aldehydes are capable of oxidizing to acids concomitantly reducing Cu^{2+} (blue) to Cu^{1+} (red ppt) (Benedict's test)
Glucose is an aldose often called "blood sugar" or "dextrose;" rotates plane-polarized light to right.
Fructose is a ketose often called "levulose;" it is a popular sweetener in beverages; rotates plane-polarized light to left
Most monomeric sugars exist as cyclic structures more than open-chain forms in solution; hemiacetals groups.
The stereochemistry about the "penultimate" carbon atom designates sugars as "D-" or "L-."
The stereochemistry about the #1 carbon atom in the ring form denotes "α-"(down) or "β -" (up)
Sugars are often modified to include amino, acetyl, or methyl groups.
Disaccharides contain two monomeric sugars; e.g, sucrose: [glucose & fructose] & lactose: [galactose & glucose]
Glucose and fructose are reducing sugars; sucrose is a non-reducing sugar.
Hydrolysis of sucrose yields equimolar mixtures of glucose and fructose often called "invert sugar."
Polysaccharides: many complex polysaccharides are polymers of glucose subunits linked by acetal functional groups.
Starch and glycogen are carbohydrates storage forms; starch [amylose] is primarily linear and is found in plants.
Glycogen is found in animals; amylopectin in plants; both contain more branching than starch and are more soluble;
Starch, glycogen, amylose, & amylopectin form hollow helixes in aqueous solution that impart a strong blue-black color to iodine molecules that insert themselves in the helix interior.

Carbohydrates (continued)
Both starch and glycogen contain α-linkages, while cellulose subunits are linked by β-linkages;
β-linkages are more suitable for optimal strength and are used for structural strength in plant cells.
Mammals lack cellulase enzymes and therefore cannot digest wood and vegetable fibers.
Complex carbohydrate structures attached to proteins on the surface of erythrocytes determine blood types.

Lipids and Cell Membranes
Structures of fatty acids, names & structures for palmitate, stearate, oleate;
Triglyceride structures in fats & oils
Phospholipids: structure, recognize common phosphoglycerides in membranes;
Sphingosine & sphingomyelin; cholesterol
Membrane structure: bilayer lipid membranes, liposomes, integral and peripheral proteins
Lateral vs. transverse diffusion
Membrane asymmetry, fluidity
Arachidonic acid is a precursor of prostaglandins; aspirin's role in reducing inflammation.

Vitamins
Vitamins are essential micronutrients.
The term "vitamin" was first used to describe the "vital amine" thiamine, which prevents Beri beri.

Water-soluble Vitamins
"B"vitamins:
- thiamine,
- riboflavin ($FADH_2$)
- pyridoxine
- niacin (NADH)
- B_{12}
- folic acid

- vitamin C (anti-scurvy, antioxidant)
- pantothenic acid (used in Coenzyme A)
- biotin (transfers activated CO_2 groups)

Fat-soluble Vitamins
- A - retinol (visual pigment)
- D – calciferol (Ca^{2+} regulation)
- E – antioxidant
- K – blood clotting (γ-carboxyglutamate)

Introduction to Metabolism
Oxidation of carbon yields free energy (-ΔG); catabolism / exergonic reactions
ATP stores energy in two anhydride linkages between phosphates
Phosphoenolpyruvate, creatine phosphate, and 1,3-bisphosphoglycerate contain high-energy bonds
ATP and creatine phosphate can be consumed in 4-5 seconds when needed.
Highly-reduced carbon atoms (more hydrogens/atom) contain more potential energy than partially oxidized ones.
NADH contains structural components including nicotinamide, ribose, adenine, phosphates ($NAD^+ \leftrightarrow$ NADH)
NADH is frequently involved in redox of alcohols and carbonyl groups (C=O); electron carrier in mitochondrial ox.
$FADH_2$ contains flavin (isoalloxazine), adenine, ribose, phosphates; redox (C-C ↔ C=C)
Coenzyme A contains ADP, pantothenic acid, β-mercaptoethylamine; carries acetyl groups as acetyl-CoA.