Study Guide, Exam 3, Chemistry 5700

Exam 3 Material: bioenergetics, catabolism, glycolysis, pyruvate oxidation, citric acid cycle

I. Here are some compounds you should **be able to name and draw structures for**:
• all glycolytic intermediates and **oxidative** pentose pathway intermediate (i.e. glucose to ribose-5-phosphate)
• The following glycolytic precursors: fructose, galactose, lactose, sucrose, glycogen, and starch
• all citric acid cycle cycle intermediates

II. Metabolic pathways: Know all the steps and stoichiometries of the reactions of the following pathways:

(a) glycolysis,
(b) feeder pathways for glycolysis from fructose, galactose, lactose, sucrose, glycogen, and starch
(c) oxidative pentose pathway
(d) citric acid cycle

III. Here are some compounds you should be able to **recognize by sight** but you need not be able to draw their structures. I will provide you with a page on the exam having the structures of each of these compounds. Be able to recognize them, and use them, if necessary, in answering exam questions (e.g. I may ask for the pyruvate dehydrogenase mechanism, in which case you will use features of NAD+, TPP, CoA, FAD and lipoamide in answering the question).
•thiamine pyrophosphate (thiazolium ring is good enough)
•lipoic acid
•NAD^+/NADH, NADP+, NADPH (know full name-i.e. oxidized or reduced nicotinamide adenine dinucleotide)
• FAD/$FADH_2$ (know full name, not just abbreviation).
• coenzyme A

IV. Catabolism terms/concepts that you should be familiar with and be able to define/explain the relevance of:
•high energy compounds-types, general structures, and properties that make them high energy compounds
•reduction potential
• strong and weak reductant and oxidant
•electron transfer reactions; single e- vs. hydride transfer
•homolytic vs. heterolytic bond cleavage
•group transfer reactions: acyl, phosphate-phosphatase, mutase, kinase, phosphodiesterase
•isomerization, elimination, rearrangement
•aldol condensation, claisen condensation
• enzymes of glycolysis, citric acid cycle
• substrate level phosphorylation
• synthase vs. synthetase
• alcohol and lactic acid fermentation
• feeder pathways for glycolysis: strategies, enzymes and routes for entry of fructose, galactose, lactose, sucrose, glycogen, and starch into glycolysis

• epinephrine, glucagon, cAMP; hormonal regulation of glycogen metabolism
• product inhibition, feedback inhibition, allosteric regulation, covalent regulation
• myocyte, hepatocyte, adipocyte
• oxidative vs. nonoxidative decarboxylation
• linear vs. cyclic pathways
• prochiral molecules

V. Writing reaction mechanisms:
• Understand the mechanisms of action and associated strategies for lowering activation energy barriers for representative enzymes of the kinase, mutase, isomerase, aldolase, dehydrogenase, and enolase families.
• Outline the mechanism of action of the α-keto acid (pyruvate, α-KG) dehydrogenase multienzyme complexes and understand the roles of the five cofactors involved. YOU NEED NOT SHOW THE CHEMISTRY OF FLAVIN OXIDATION/REDUCTION FOR THIS EXAM, BUT DO NEED TO BE ABLE TO SHOW THE CHEMISTRY OF THE OTHER COFACTORS.
• Understand how general acids/bases, electron sinks, metal ions, phosphoenzyme intermediates, etc. contribute to the mechanisms of enzymes of glycolysis, and citric acid cycle.
• Recognize/explain the importance of the following mechanistic terms: nucleophile, electrophile, cis-enediolate, Schiff base, tetrahedral and pentavalent intermediates, keto/enol tautomerization, control of sterochemical outcome (cis vs trans, R vs S, pro R vs Pro S)

VI. Problem solving-
•Be able to use the Nernst equation, gibb's free energy equation, equilibrium constants, and tabulated E° and ΔG° values to calculate electromotive force/free energy values for reactions under standard state and nonstandard state conditions. **I will provide you equations and constants.** See examples from your text, the quizzes, and previous exams. You will <u>not</u> be asked to work any problems involving change in temperature or pH.
Recall ΔG° values are additive when adding reactions, while equilibrium constants are multiplicative (multiply Keq values) when adding reactions.

VII. Oxidation numbers- Use the rules I provided in class to assign oxidation numbers to individual atoms of compounds from glycolysis and the citric acid cycle. Assign oxidation numbers as a means of "electron bookkeeping" in oxidation/reduction reactions.