

# Review Guide for Third Exam in Biochemistry 507 (1997)

## Lecture 23: Thermodynamics in Biology

1. Free energy, enthalpy, entropy, and the equations that relate them. You should be able to work simple quantitative problems in which you determine the standard free energy change for a reaction from its equilibrium constant, or the  $K_{eq}$  from the standard free energy change.
2. Understand and be able to use the equation that relates free energy change for a reaction to the standard free energy change and the concentrations of reactants and products. For any problems on the exam, I will supply the value of the gas constant R, but not the equations.
3. Understand the chemical explanations for the relatively high standard free energy changes for hydrolysis of PEP, 1,3-bisphosphoglycerate, ATP, and creatine phosphate. I do not expect you to remember any values for standard free-energy changes except that for ATP (–30.5 kJ/mol).

## Lecture 24: Chemical Sense in Metabolic Pathways

1. Be able to define: homolytic and heterolytic reactions;  $S_N1$  and  $S_N2$  nucleophilic substitutions, carbocation and carbanion.
2. Thioesters: the basis of their high standard free energy of hydrolysis.

## Lecture 25: ATP and Phosphoryl Group Transfers

1. Structures of phosphate mono- and di-esters, phosphate anhydrides.
2. Be able to describe the experimental evidence that in the hydrolysis of glucose-1-phosphate, a phosphoryl, not a phosphate, is transferred to water.
3. ATP: be able to give examples of reactions in which the  $\alpha$ ,  $\beta$ , and  $\gamma$ , phosphates are the sites of attack.
4. Kinases: definition of this class of enzymes; describe how a phosphoenzyme intermediate acts in the kinase reaction.

## Lecture 26: Electron Transfers in Biology

1. Be able to solve simple problems that involve predicting the spontaneous direction for a redox reaction, given the two half-reactions.
2. Be able to calculate the standard free energy change for a redox reaction, given the standard reduction potentials for the two half-reactions.
3. Be able to describe the experimental setup for measuring standard reduction potentials.
4. Dehydrogenases: know the structure of the oxidized and reduced nicotinamide moiety of NADH. Understand the use of UV spectrophotometry in measuring the rate of an NADH-linked reaction.

### **Lecture 27: Glycolysis**

1. Know the structure of each intermediate from glucose to pyruvate, the name of each enzyme on that path, and know the role of the cofactors NAD and ATP in the path.
2. Understand the action of glycogen phosphorylase in the breakdown of liver glycogen; the reaction itself, the way in which branches are degraded.
3. Be ready to explain the requirement for  $Mg^{2+}$  ion in glycolysis reactions.
4. The first and second stages of glycolysis: where is ATP invested, where is it gained, and how much net gain is there?
5. Regulation of PFK-1: what are the regulators, and why does each make biological sense.
6. Mechanism of glyceraldehyde phosphate dehydrogenase, at the level of detail discussed in class.

### **Lecture 28: NADH Recycling and Fermentation; Pentose Phosphate Pathway**

1. Alternative fates of pyruvate under aerobic, anaerobic conditions
2. Role of lactate dehydrogenase in NADH recycling
3. Role of alcohol fermentation in yeast anaerobic metabolism
4. Two important products of hexose monophosphate pathway
5. Mechanism of detoxification by glucuronidation

### **Lecture 29: Pyruvate Oxidation and the Citric Acid Cycle**

1. Pyruvate dehydrogenase complex: the reaction it catalyzes, the role of each cofactor, and the series of steps that occur on the enzyme.
2. Know each intermediate of the citric acid cycle, each cofactor, and the enzyme that catalyzes each step.
3. Be ready to describe the analogy between the  $\alpha$ -ketoglutarate dehydrogenase reaction and the pyruvate dehydrogenase reaction at the level of chemical mechanism.

### **Lecture 30: Anaplerotic Reactions and the Glyoxylate Cycle**

1. Pyruvate carboxylase reaction: reaction, role
2. Biotin: structure of the "business end" and of the carboxyl intermediate
3. The general role of anaplerotic reactions; under what conditions are these reactions important?
4. Two enzymes and reactions unique to glyoxylate cycle
5. How does glyoxylate cycle allow carbohydrate synthesis from fats?

### **Lecture 31: Oxidation of Fatty Acids**

1. Steps in the digestion of lipids in the diet and transport of fatty acids to the liver
2. Steps in the mobilization of fatty acids stored in adipose tissue
3. Three stages of fat oxidation
4. Activation of fatty acids: the reaction
5. Transport of FA into mitochondria; role of carnitine
6. The four-step process of  $\beta$  oxidation: know the structures of the intermediates, the electron carriers for each oxidation step, and the localization of the enzymes of this pathway within the cell
7. The path from propionyl-CoA to the citric acid cycle; be able to show the intermediates and know the cofactor requirements for the path
8. Structure, role of the ketone bodies; circumstances under which they are overproduced

### **Lecture 32: Transamination and the Urea Cycle**

1. Know the general reaction catalyzed by transaminases
2. Be able to describe in chemical detail the role of PLP in transamination
3. The reaction catalyzed by glutamate dehydrogenase
4. The reactions in the synthesis of carbamoyl phosphate
5. The sequence of steps, and the names (not structures) of the intermediates of the urea cycle
6. The reaction catalyzed by arginase (structures)
7. Role of the urea cycle in mammals

### **Lecture 33: Oxidation of $\alpha$ -keto acids**

1. Role of tetrafolate in carrying one-carbon units; detailed structure of the cofactor not essential
2. Be able to trace the path from each of these amino acids to the citric acid cycle (reactions, structures, coenzymes): aspartate, asparagine, glutamate, glutamine, alanine, proline, arginine
3. Be prepared to explain the analogy between the reaction sequence by which a branched chain  $\alpha$ -keto acid (say that derived from isoleucine) is oxidized with the pathway of pyruvate oxidation and with the  $\beta$ -oxidation pathway for fatty acids.
4. Know the definition and significance of glucogenic and ketogenic amino acids