

The following numeric information may be useful

$$R = 2.0 \text{ cal/(mole.degree)}$$

$$F = 23 \text{ kcal/(mole.volt)}$$

$$G^{\circ} \text{ for ATP/ADP} = -7.4 \text{ kcal/mole.}$$

$$G^{\circ} \text{ for CrP/Cr} = -10.4 \text{ kcal/mole}$$

$$P_K = 1,$$

$$P_{Na} = 0.01$$

$$P_{Cl} = 0.5$$

The free energies of formation of standard solutions of glucose and fructose are -219.2 and -218.8 kcal/mole, respectively.

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1. A Draw the structure of glucose using either a ring or straight chain representation. Explain how (i) mannose and (ii) galactose differ from glucose. Which are (a) epimers; (b) enantiomers; (c) diastereomers?

B. A hypothetical hexasaccharide was subjected to chemical analysis and the following data obtained:

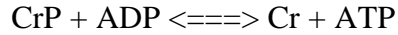
- a.) No reaction was obtained with Fehling's reagent.
- b.) Following hydrolysis with dilute acid only glucose could be detected.
- c.) Upon methylation and hydrolysis the reaction mixture contained
 - 2 2,3,4,6 tetramethyl glucose
 - 4 2,3, 6 trimethyl glucose.

What can you deduce about the structure of the hexasaccharide?

C What do you expect would be the overall shape of a polysaccharide that has alternating (1 4) and (1 4) glycosidic bonds? Explain your answer.

2. A. The free energies of hydrolysis of glucose-6-phosphate and fructose-6-phosphate are both -13.8 kcal/mole. What is the equilibrium constant for the reaction catalyzed by phosphohexose isomerase (G-6-P \rightleftharpoons F-6-P)?

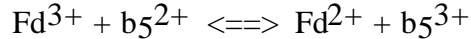
B. Calculate ΔG at 37°C for the reaction



under conditions that actually exists in the cytoplasm of neurons, i.e. CrP = 4.7 mM, Cr = 1.0 mM, ADP = 0.2 mM and ATP = 2.6 mM (Cr = creatine, CrP = creatine phosphate).

C. Ferredoxin (Fd) is an iron containing protein present in the photosynthetic apparatus; during photosynthesis the iron undergoes a 1-electron redox reaction with an $E^{\circ} = -0.42\text{v}$. Similarly cytochrome b₅ is an iron-protein present in the microsomes with an $E^{\circ} = 0.0\text{ v}$.

For the reaction at pH = 7



Where does the equilibrium lie? Why?

- (a) Very much to the right?
- (b) A little to the right?
- (c) About in the middle?
- (d) A little to the left?
- (e) Very much to the left?

D. It is possible to prepare cell sacs in which the internal contents have been replaced by a solution of your choice. You fill the sac with 400 mM KCl and 10 mM NaCl. You place this sac into a medium with the composition 10 mM KCl + 400 mM NaCl, What is the membrane potential that is immediately developed at 37°C?

3. Because grapes make their own sugar it occurred to Gallo Vineyards that the fermentation of grape juice to wine by glycolysis could proceed effectively without the participation of sugar phosphates. This being the case they hired Creative Biochemists Inc. to design an improved glycolytic pathway for the formation of alcohol from glucose. CBI investigated this problem and reported that such a pathway could be designed: this pathway is characterized by being significantly shorter but would require that the **specificity** (but not the **reaction catalyzed**) of all remaining enzymes would have to be changed.

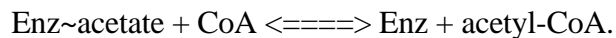
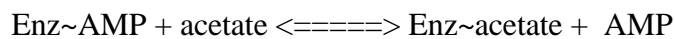
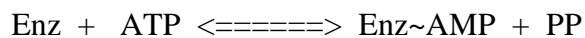
Using chemical structures or names propose such a pathway. Name the enzymes that you utilize

Does the resulting **overall** reaction differ in any way from traditional glycolysis?

4. You set up the following incubations with fresh yeast juice which has been thoroughly dialyzed. In each case deduce the compounds which accumulate in the reaction mixture.

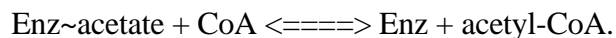
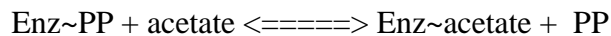
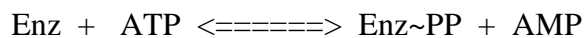
- a) Glucose with an equal molar amount of ATP.
- b) Glucose-1-phosphate with an equal molar amount of ATP.
- c) Dihydroxyacetone phosphate + NADH.
- d) Fructose biphosphate + NAD⁺
- e) Glucose with excess ATP and an equal molar amount of NAD⁺

5. Your neighborhood enzymologist has just purified a new enzyme which synthesizes acetyl CoA from acetate + ATP. At equilibrium the reaction mixture contains some AMP + PP. The following 3-step mechanism is proposed:



Using exchange reactions how would you:

(1) Distinguish this reaction from the plausible alternative



(2) Verify the individual steps of the first sequence.