1. See p V-1 of classnotes for structure. The hydrolysis releases ca 2/3 of a proton. Proton production at pH = 7 is worth -9.5 kcal/mole (Justified in additional reading of Ch. IV). 2/3 of -9.5 = -6.5 which is > 80% of -7.6.

2. Orient the NADH with the amide on the right. The two C4 hydrogen atoms point at you and away from you. Label the one pointing at you with D. Apply the CIP rules. The D occupies the R position so the original H is proR.

3. (i) Orient NADH as in 2. Place acetaldehyde between you and the NADH, oriented with the C=O pointing at 12 o'clock and the methyl on the right. (See V-10 for si face of acetaldehyde)

(ii) Use ethanol completely labeled in the methylene group with deuterium and use this ethanol to make NADD using alcohol dehydrogenase. Then incubate this NADD with pyruvate and lactic dehydrogenase, isolate the lactate and see if it contains D. Yes=A.

4. Classroom rule. Addition to re face gives proR if product is prochiral but if the product is chiral you must figure it out explicitly because the incoming substituent will have a different priority than the original substituent (otherwise the product would not be chiral). Addition of H to the re face of pyruvate yields S-lactate.

5. See Fig VI-4a of class notes.

This is a trick There is no such compound as G-1,6-diP (except as an intermediate of phosphoglucomutase). If the substrate were G-1-P the products would be CHO-CH2OH and CHO-CHOH-CHOH-CH2OP. Cleavage of the aldohexose would require separate paths for metabolizing the 2C compound and the 4C compound.

6. (i) Iodoacetate blocks glyceraldehyde-3-P dehydrogenase. But its not DHAP and 3-PGA that are the major product because the aldolase reaction is strongly biased in favor of F-1,6-bisP.

(ii) Pyruvate, NADH and ATP.

7. Relative to glucose the OH at C4 of galactose is inverted; C4 becomes CHO of 3-PGA. The stereochemistry is lost at this point. So use galactose based sugars (in ring form) up to and including the aldolase reaction and regular glycolysis thereafter. (What is the keto sugar that is formed?)

8. C3 ⇒ CH2OH of DHAP ⇒ CHO of 3-PGA; C4 ⇒ CHO of 3-PGA. So the label appears in only the CHO of 3-PGA. This becomes the COOH of pyruvate. The COOH is eliminated as CO2 by pyruvate decarboxylase. All the radiolabel is lost as CO2. With muscle the radiolabel appears in the COOH of lactate. In air all of the radiolabel appears as CO2.

When the initial label is in C1 this becomes the CH2OP of 3-PGA which becomes the methyl of pyruvate and then lactate and ethanol as appropriate. In air all is lost as CO2.

9. (i) pyruvate + NADH + H⁺ ⇋ lactate + NAD⁺

\[ \Delta E^{o'} = -0.2 + (0.32) = 0.12 \text{ volt} \]

\[ K = \exp(nF\Delta E^{o'}/RT) = \exp((2)(23500)(0.12))/((2)(300))) \]

~ 12,000

The pH dependence of NAD = -0.03 v/pH; for the pyruvate/lactate couple (2e + 2H⁺) it is -0.06 v/pH. So the new values for the individual couples are -0.35 and -.26 respectively. \( \Delta E^{o'} = 0.09 \).

K ~ 1200

(ii) \[ \Delta G = \Delta Go' + RT \ln \frac{[NAD][lactate]}{[NADH][pyruvate]} \]
\[ \Delta G = -nF\Delta E = -2(23.5)(0.12) = -5.6 \text{ kcal/mole}. \] When NAD/NADH = 1 & pyruvate/lactate = 1 the In term is 1 and \( G = G_0' \) and \( E = E_0' \).

When NAD/NADH = 160 & pyruvate/lactate = 1/160 the In term is 160 \times 160 and \( \Delta G = 0.6 \text{ kcal/mole} \).

10. (i) Both are examples of the aldehyde-keto interconversion. So represent \( C_3-C_6 \) of glucose by \( R \) and \( C_3 \) of DHAP by \( R \) and simply work your arrows on the top two carbons in each case. Remember that these reactions are the enzyme-catalyzed equivalent of the Lobry de Bruyn etc. reaction that occurs at high pH in the absence of enzymes.

(ii) One would get the same product, namely F-6-P because \( C_2 \) is now the C=O and it doesn't matter if you started with mannose or glucose.

11.

12. For typing convenience I use \( A \) to represent cytochrome c and \( B \) to represent cytochrome c1.

The reaction is:

\[ A^{+2} + B^{+3} \leftrightarrow A^{+3} + B^{+2}. \]

\[ K = \frac{[A^{+3}][B^{+2}]}{[A^{+2}][B^{+3}]} = \frac{[8][8]}{[2][7]} = 4.6 \]

\[ \frac{RT \ln K = (2)(300)(1.5)}{nF} = (1)(23500) = 0.038 \ v. = (-0.26) + E_0'(c1). \]

\[ E_0'(c1) = 0.298 v \]

As both \( c \) and \( c_1 \) are "simple" Fe compounds neither uses protons so the value is pH independent.