

Recitation #05 Problems

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QUESTION WARM UP 1 (Gumport 8-3)

The enzyme hexokinase catalyzes the following reaction:



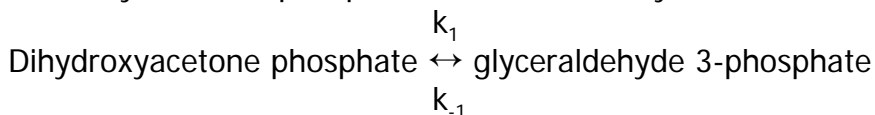
For this reaction, $\Delta G^{\circ'} = -4.0 \text{ kcal/mol}$.

- Calculate the change in free energy $\Delta G'$ for this reaction under typical intracellular conditions using the following concentrations: glucose, 55mM; ATP, 5.0 mM; ADP, 1.0 mM; and glucose 6-phosphate, 0.1 mM. Assume that the temperature is 25° C. ($R = 1.98 \times 10^{-3}$)
- In the typical cell, is the reaction catalyzed by hexokinase close to equilibrium or far from equilibrium? Explain.

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QUESTION 1 (Gumport 8-8)

The enzyme triose phosphate isomerase catalyzes the following reaction:



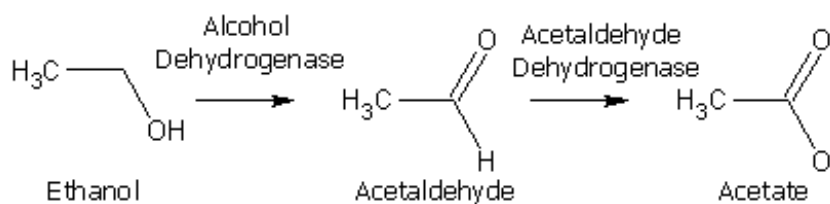
The $\Delta G^\circ'$ for this reaction is 1.83 kcal/mol. In light of this information, which of the following statements are correct?

- (A) The reaction would proceed spontaneously from left to right under standard conditions.
- (B) The rate of the reaction in the reverse direction is higher than the rate in the forward direction at equilibrium.
- (C) The equilibrium constant under standard conditions favors the synthesis of the compound on the left, dihydroxyacetone phosphate.
- (D) The data given are sufficient to calculate the equilibrium constant of the reaction.
- (E) The data given is sufficient to calculate the left-to-right rate constant (k_1).

QUESTION 2 (Exam 2, 2002)

The breakdown of ethanol in the liver is catalyzed by the enzyme alcohol dehydrogenase to form acetaldehyde, and the acetaldehyde is then broken down by acetaldehyde dehydrogenase into acetate in the simplified reaction shown below:

Accumulation of acetaldehyde leads to facial flushing and sensations of discomfort. Some people have the "A" form of acetaldehyde dehydrogenase and others have the "B" form, which is 100 times slower than the "A" form.



- (A) Draw a diagram of the reaction coordinate for the un-catalyzed reaction, and for the reaction catalyzed by the "A" form and for the "B" form of the enzyme.
- (B) If the activation energy of for the un-catalyzed breakdown of acetaldehyde into acetate, ΔG^\ddagger , is 14 kcal/mol, and the reaction catalyzed by the "A" form proceeds 106 times more rapidly at 25° C, what are the ΔG^\ddagger for the reaction catalyzed by the "A" form and by the "B" form?

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QUESTION 3 (Gumport 8-5)

The text states that a decrease of 1.36 kcal/mol in the free energy of activation of an enzyme-catalyzed reaction has the effect of increasing the rate of increasing the rate of conversion of substrate to product by a factor of 10. What effect would this decrease of 1.36 kcal/mol in the free energy of activation have on the reverse reaction, the conversion of product to substrate? Explain.

QUESTION 4 (Gumport 8-8)

The simple Michaelis-Menton model applies only to the initial velocity of an enzyme-catalyzed reaction, that is, to the velocity when no appreciable amount of product has accumulated. What feature of the model is consistent with this constraint? Explain.

QUESTION 5

Assuming Michaelis-Menten kinetics apply sketch the graphs of

- (A) V vs [S]
- (B) V vs [ET]
- (C) [S] vs Time
- (D) [P] vs Time

QUESTION 6: (Gumport 8-17)

If you were studying an enzyme that catalyzed the reaction of ATP and fructose 1-phosphate to form fructose 1,6-bisphosphate and ADP and discovered that a plot of the initial velocity of formation of fructose 1,6 bisphosphate versus ATP concentration was not hyperbolic, but rather sigmoid, what would you suspect?

QUESTION 7: (Gumport 9-19)

True or False & Why:

Which of the following are roles for Mg^{2+} in reactions that use ATP as a phosphoryl donor, for example, the NMP kinases?

- (A) Mg^{2+} binds to the enzyme and activates a water molecule
- (B) Mg^{2+} neutralizes partially the negative charge on the triphosphate group of the ATP.
- (C) Mg^{2+} forms a stable conformation of ATP by binding to its phosphoanhydride "tail"
- (D) Mg^{2+} provides potential binding points on the ATP for the enzyme to recognize.

QUESTION 8: (Gumport 9-8)

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If you introduced a mutation into adenylate kinase that prevented P-loop movement and subsequent lid closure, what reaction would you expect the enzyme to catalyze when incubated with AMP and ATP?

QUESTION 9:

Draw the intermediate in the NMP Kinase mechanism.

QUESTION 10: (From Exam 4, 1995)

Draw a typical oxygen binding curve for hemoglobin within red blood cells. Label the axes. Indicate and label a curve that would result if you added a molecule that shifted the allosteric equilibrium towards the T state.

QUESTION 11: (Gumport 10-7)

An effective respiratory carrier must be able to pick up oxygen from the lungs and deliver it to the peripheral tissues. Oxygen dissociation curves for substances A and B are shown below. (A on left, B on right) What would be the disadvantage of each of these substances as a respiratory carrier? Where would the curve for an effective carrier appear in the figure?

