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Chemistry 130A - Midterm 1

50 minute open book exam

September 27, 1993

Read the whole test, then do the easiest parts first.

1. (25 points)

During exercise glycogen—a polysaccharide—is hydrolyzed to produce glucose ($C_6H_{12}O_6$) which is converted to pyruvate by a series of enzyme-catalyzed reactions. The pyruvate is then oxidized to CO_2 and H_2O by steps in the citric acid cycle. The net reaction can be approximated by

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l)$$

a. Use the Tables in the book to calculate ΔH^o for this reaction at 25 °C, 1 atm.

b. Use the Tables in the book to calculate ΔS^o for this reaction at 25 °C, 1 atm.

c. Calculate ΔG^o for this reaction at 37 °C, 1 atm. You may assume that ΔH^o and ΔS^o are independent of temperature.

d. In the body the reaction does not occur with solid glucose reacting with 1 atm of O_2 gas to form 1 atm of CO_2 gas and pure water. The main difference in the body is that the glucose is in very dilute solution. Will the free energy for the reaction under these conditions be greater or less than your answer in part (b)? Explain in a few sentences or equations or both.

e. The answers to (a) and (b) are in kjoules, but we usually think of food energy in terms of kcal. The glycogen in our bodies came from eating, of course. If all the energy in a teaspoon of sugar (15 kcal) could be converted into work by our muscles, how many times could we lift a weight of 1 pound (mass = 0.454 kg) by 1 foot (distance = 0.305 m).

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2. (25 points)
The isomerization of 3-phosphoglycerate to 2-phosphoglycerate is an important step in the metabolism of glucose.

$$3\text{-PG} \rightarrow 2\text{-PG}$$

At pH 7, 25 °C its equilibrium constant is K = 0.156.
a. What is the standard free energy for the reaction (kJ) at 25 °C?

b. What is the free energy change (kJ) of the reaction when both concentrations are equilibrium concentrations at 25 °C?

c. What is the free energy change (kJ) of the reaction when the concentration of 3-PG = the concentration of 2-PG?

d. In a certain cell the concentration of 3-PG = 5.3×10^{-5} M. Calculate the maximum concentration of 2-PG which will allow the reaction to occur.

e. Write the equation you would use to calculate ΔH^o for the reaction from equilibrium constants. If K increases with increasing temperature, what is the sign of ΔH^o? Is heat given off or absorbed by the reaction?

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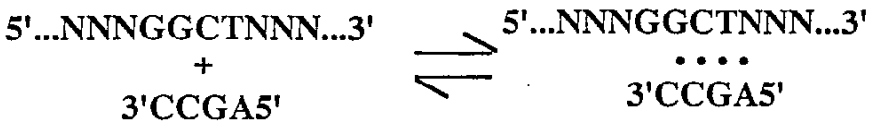
3. (25 points)
You want to estimate the concentration of a probe necessary to find the sequence 5'-GGCT-3' in a target DNA molecule. Use the nearest-neighbor values in the handout sheet to calculate thermodynamic data for the formation of a DNA double strand at 25 °C from the probe 5'-AGCC-3' and the DNA molecule. You can ignore the effect of the dangling ends—the NNN.



(a) Calculate ΔG^o at 25 °C.

(b) Calculate the equilibrium constant K at 25 °C.

(c) Write a mass balance equation for the target DNA in terms of concentration of free DNA at equilibrium [DNA], complex concentration [complex], and total DNA [DNA_o]. Write a mass balance equation for the probe molecule in terms of [probe], [complex], [$probe_o$].

(d) Using K from part (b) calculate the concentration of probe necessary to bind 1/2 of the DNA 5' -GGCT-3' sites. The concentration of the probe is much larger than the concentration of the DNA sites. This means that the concentration of probe added to the solution is equal to the free concentration of probe at equilibrium.

(e) What if the DNA molecule had the probe sequence 5'-AGCC-3' somewhere else in its sequence? Would this increase or decrease the concentration of added probe necessary to bind half the target sequence? Explain qualitatively.

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4. (25 points)

(a) Calculate the change in entropy (J K^{-1}) for a new deck of 10 cards which is shuffled thoroughly. Its initial state is ordered (1, 2, ...9, 10); its final state is disordered.

(b) Calculate the change in entropy (J K^{-1}) when 0.80 mol of N_2 (gas) is mixed with 0.20 mol of O_2 (gas) to make 1 mol of air.

(c) A spontaneous reaction occurs at constant temperature and pressure. For each thermodynamic variable (ΔS, ΔH, ΔG, ΔE) state whether its sign is positive, negative, zero, or impossible to tell.

(d) Christian Anfinsen received the Nobel Prize for showing that an enzyme (ribonuclease—RNAase) could be completely denatured—unfolded, and then refolded to regain the same active enzyme. The reaction was done at 1 atm pressure:

active RNAase (pH 7, 25 °C) → denatured (8 M urea, 90 °C) →active RNAase (pH 7, 25 °C)

Calculate ΔS, ΔH, ΔG, ΔE for the complete reaction as written.

(e) The statement "You can't unscramble an omelette to make an egg." is a qualitative description of the second law of thermodynamics. Yet you can feed the omelette to a hen and have her metabolically convert the omelette into an egg. Does this mean that hens are not limited by the second law? Answer yes or no and give a one sentence explanation.