Fall, 2014, 0101

**Biochemistry 463, ~~[illegible]~~**
**University of Maryland, College Park**
**Biochemistry and Physiology**
**Exam I (100 points total)**

**Your Name:** Key
**Your SID #:**

**Prof. Jason Kahn**
**October 1, 2014**

**You have 53 minutes** for this exam.

**Exams written in pencil** or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. Use the extra space on the last page if you need more space.

**You will need** a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, *i.e.*, if you don't know, guess.

| | | |
|---|---|---|
| $\Delta S_{system} - \Delta H_{system}/T \geq 0$ | $p\text{H} = -\log([\text{H}^+])$ | $R = 8.314$ J/mol K |
| $S = k\ln W$ | $\Delta G = \Delta H - T\Delta S$ | $p\text{H} = pK_a + \log([\text{A}^-]/[\text{HA}])$ |
| $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$ | $\Delta G^{\circ\prime} = -RT\ln K'_{eq}$ | $\Delta G = \Delta G^{\circ\prime} + RT\ln Q$ |

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

## 1. (20 pts) Thermodynamics

(a; 5 pts) Starting from two of the equations above, show that ΔG < 0 when Q < K for a reaction.

$\Delta G = \Delta G^{\circ\prime} + RT\ln Q$ (+1)

sub $\Delta G^{\circ\prime} = -RT\ln K'_{eq}$ (+1)

$\Delta G = -RT\ln K'_{eq} + RT\ln Q$ (+1)

$= RT(\ln Q - \ln K'_{eq})$

$\Delta G = RT\ln\left(\frac{Q}{K'_{eq}}\right)$

So if $Q < K$,

(+2) $\ln Q/K'_{eq} < 0$ and

$\Delta G < 0$

Score for the page 5

(b; 5 pts) Circle all of the true statements below (i)-(ii)-(iii). Explain your reasoning.

(+2) (i) $\Delta G°'$ for each step of an operational biochemical pathway must be negative. → no – indep of [ ]

(ii) $\Delta G$ for each step of an operational biochemical pathway must be negative.

(iii) $K_{eq}'$ for each step of an operational biochemical pathway must be ~~<~~ 1. >1

(+3) The actual free energy change $\Delta G$ must be < 0 for the flux for each reaction to be in the forward direction – if a reaction has $\Delta G \geq 0$ the net flow will be backward or zero.

(c; 10 pts) The biochemical standard state free energy changes for phospho*enol*pyruvate (PEP) hydrolysis and ATP hydrolysis are as follows:

ATP + $H_2O \rightleftharpoons$ ADP + $P_i$ + $H^+$ $\Delta G°' = -30.5$ kJ/mole at 298 K

PEP + $H_2O \rightleftharpoons$ pyruvate + $P_i$ $\Delta G°' = -61.9$ kJ/mole at 298 K

Calculate $K_{eq}'$ at 298 K for the phosphorylation of ADP by PEP to give ATP + pyruvate. Remember that because we are assuming pH 7, the concentration (formally, the activity) of $H^+$ relative to its standard state is 1. (The activity of water is also taken as 1.)

PEP + ADP + $H^+ \rightleftharpoons$ ATP + pyruvate $K'_{eq} = ?$

Add reactions, reversing the first one (+1)

ADP + $P_i$ + $H^+ \rightleftharpoons$ ATP + $H_2O$ $\Delta G°' = +30.5$ kJ/mole

PEP + $H_2O \rightleftharpoons$ pyruvate + $P_i$ $\Delta G°' = -61.9$ kJ/mole

PEP + ADP + $H^+ \rightleftharpoons$ ATP + pyruvate $\Delta G°' = -31.4$ kJ/mole (+3)

(+1) $K'_{eq} = e^{-\Delta G°'/RT} = e^{-(-31400\ J/mole)/(8.314\ \frac{J}{mol\ K} \cdot 298 K)}$ (+2)

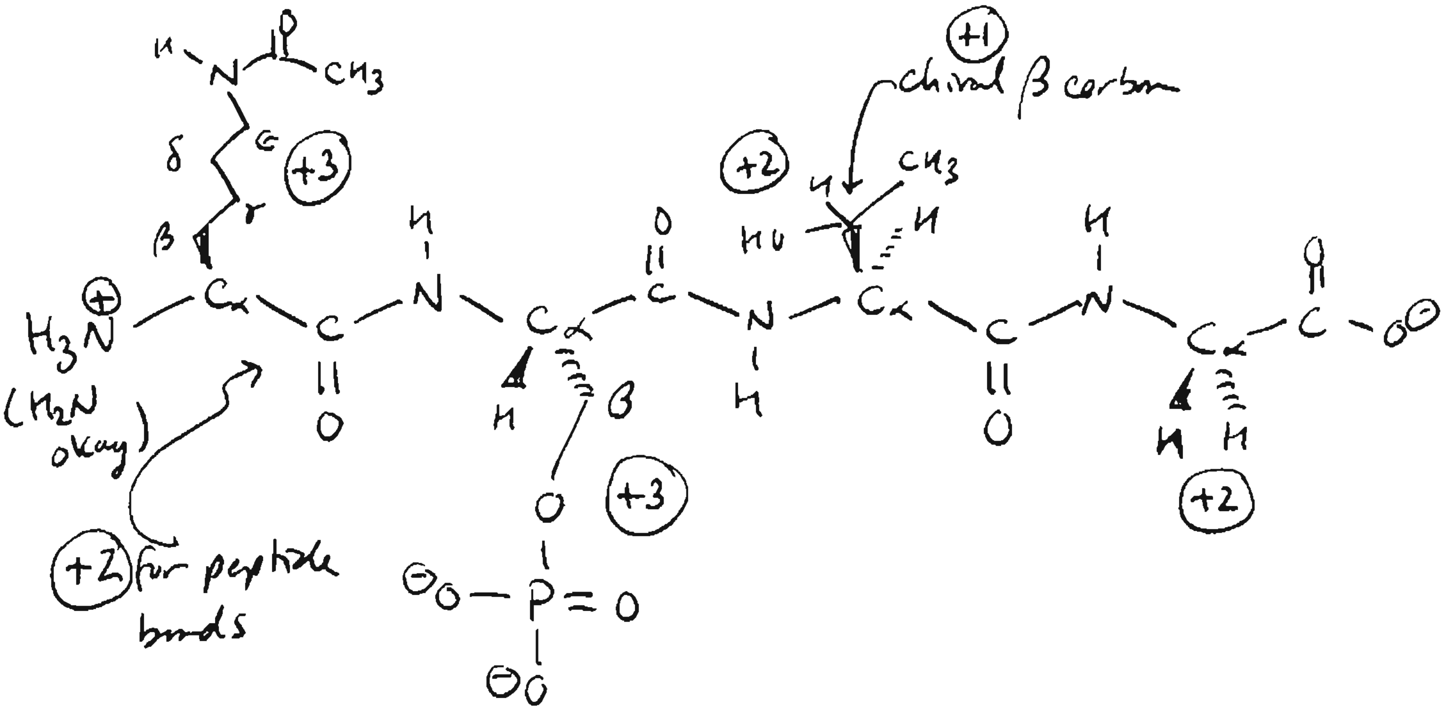
(b/c $\Delta G°' = -RT \ln K'_{eq}$) $= e^{(31400/(8.314 \times 298))} = e^{12.67} \approx 3.18 \times 10^5$ (+3)

Score for the page /15

**2. (20 pts) Protein Structure**

The sequence KSTG is found within the solvent-exposed N-terminal tail of the DNA packaging protein Histone H3, and it is frequently modified during gene regulation.

- Draw the structure of (OAc-K)(P-S)TG, which is KSTG with the Lysine being acetylated at the ε-amino group and the Serine being phosphorylated.
- Assume all *trans* peptide bonds, give correct stereochemistry for C-α's, and identify the chiral side chain carbon; you don't need to draw the correct stereochemistry at that carbon. (+2)
- The $pK_a$'s of the phosphate in P-Ser are about 2 and 6. The pKa of the N-terminal $-NH_3^+$ is 8. In your diagram, show the P-Ser in its predominant form at pH 8.
-
- Estimate the average total charge on the peptide at pH 8: -2.5 (+3)
-
- Estimate the charge of the unmodified KSTG peptide at pH 8: +0.5 (+2)




pKa's = 2, 6 so deprotonated

Charge at pH 8 (= pKa for N-terminal $-\overset{+}{N}H_3$)

+½ 0 -2 -1

For KSTG:

+½ +1 0 -1

Score for the page /20

**3. (20 pts) Carbohydrates**

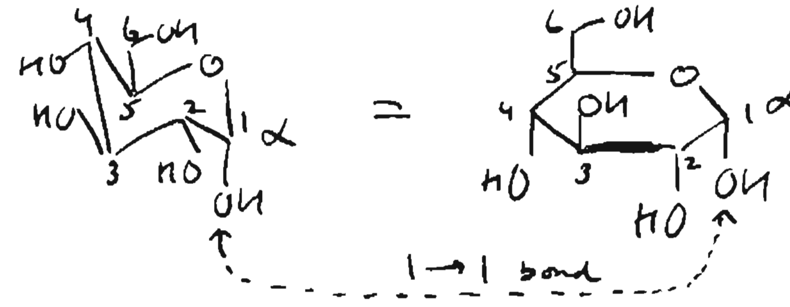
The disaccharide trehalose, ***O*-α-D-glucopyranosyl-(1→1)-α-D-glucopyranose**, has a variety of biological functions in different organisms. For example, trehalose is used for energy storage in insect flight muscle, which have the highest power output (energy produced per unit time) of any tissue. The glycosidic linkage is hydrolyzed by the enzyme trehalase.

- Draw a Haworth projection and a physically reasonable chair structure for trehalose. Number the carbons. 9 5
- 4 Speculate on why trehalose might be used in preference to glycogen in insect flight muscle.
- 2 List two other essential functions of carbohydrates besides their use as fuel.

(+1) structure as in cellulose

(+1) information/recognition as in glycoproteins [examples not needed]

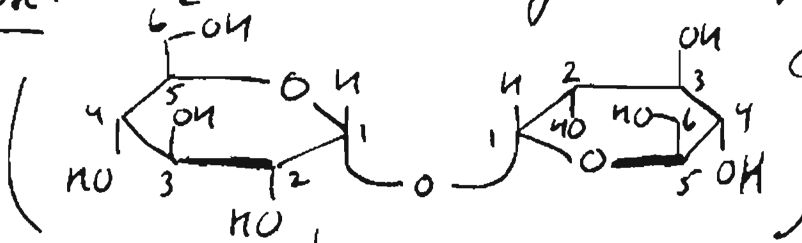
Glucose




Trehalose:

(+2) for glucose Haworth

(+1) for numbering any one ring

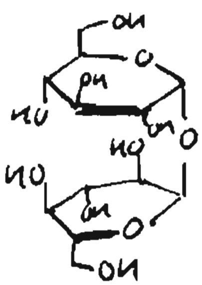


180° from chair

(+3) for α(1→1)α linkage

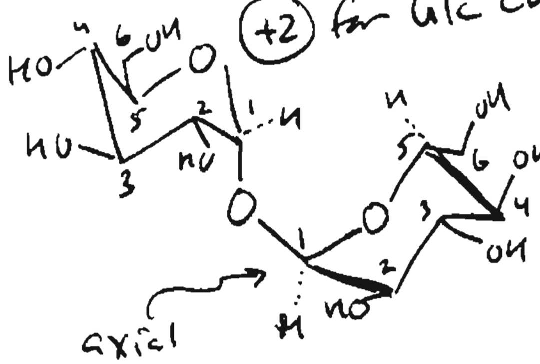
(+3) for correct Haworth for 2nd ring - need #'s on only one

or



(+1) – Hydrolysis of trehalose gives 2 × glucose w/ one cleavage ⇒ rapid availability of (+3) glucose for active metabolism

(+2) for Glc chair w/ α anomer



(+3) for ~~reasonable~~ correct 2nd chain

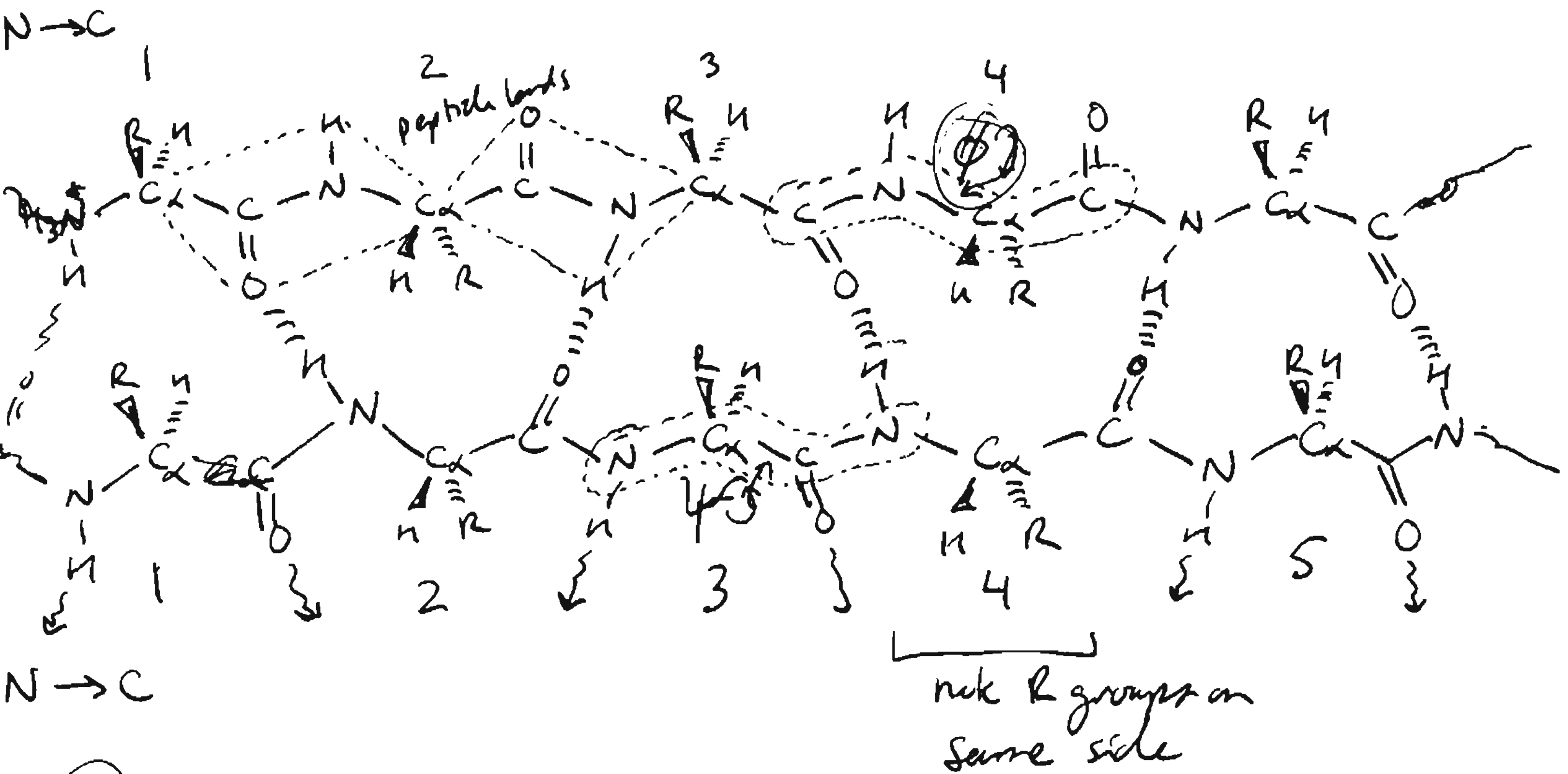
axial

Score for the page /20

**4. (25 pts) Secondary Structure in Proteins**

- List the two essential structural characteristics of stable secondary structures discussed in class.
- Sketch the hydrogen bonding pattern in a parallel β sheet, showing five residues of each of two strands. Show α carbon stereochemistry. Represent side chains as R. Don't write too large!
- On your diagram, circle the four atoms that define the Phi (Φ) torsion angle for any one residue and the four atoms that define Psi (Ψ) for another residue.
- Based on your picture, explain why β sheet structures are found in the upper left of the Ramachandran diagram (one sentence will do, not a trick question).
- Name a program used for 3-D visualization of biomolecules.

(+4)
- All H-bond valences satisfied for backbone
- Any side chain (except Pro) can be accomodated




(+2) for peptides
(+2) for parallel
(+4) for H-bonding pattern
(+2) for stereochemistry
(+2) for $\phi$
(+2) for $\Psi$

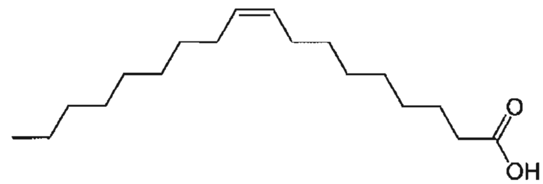
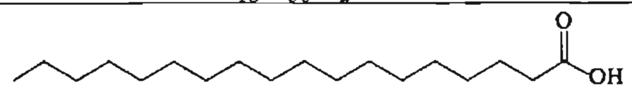
(+4) The β-sheet is nearly an <u>extended structure</u>, so $\phi$ and $\Psi$ are in the neighborhood of −180, +180 (~ −120, +120)

(+2) Pymol, Rasmol, Jmol, Molmol, King, Kinemage etc.

Score for the page ______ /25

**5. (15 pts) Lipids and Redox**

Consider oleic acid vs. stearic acid. The table gives their structures, densities, and standard enthalpies of combustion, $\Delta H^\circ_c$, essentially a measure of caloric content.

| | Oleic Acid, $C_{18}H_{34}O_2$ | Stearic Acid, $C_{18}H_{36}O_2$ |
|---|---|---|
| Structure |   |   |
| Density | 0.895 g/ml | 0.941 g/ml |
| $\Delta H^\circ_c$ | –11161 kJ/mol | –11291 kJ/mol |

- Explain why oleic acid has a lower density than stearic acid.
- Explain why oleic acid has a lower heat of combustion than stearic acid, and why both of them have larger heats of combustion per carbon atom than glucose ($\Delta H^\circ_c$ = –2805 kJ/mol).

– Oleic acid has a lower density (greater volume per molecule) because the cis d.b. (+2) means that the chains cannot (+3) pack as efficiently as the straight-chain stearate alkyl group. The 2 H's would make only a <1% difference in mass, vs. a ~5% change in density

– Stearic acid is fully reduced (+3) so there are two more $e^-$ (+2) available to give to $O_2$ than there are in oleic acid.

[Stearic acid C's have total ox # = −32, gives up 104 $e^-$ in making 18 $CO_2$
Oleic acid C's " " " " = −30, " " 102 $e^-$ " " "
Difference in $\Delta H_c$ is ~1.2%

– The carbons in glucose have an average oxidation # of 0 (+2) so they can only give up 4$e^-$ per carbon (+3) to $O_2$ as opposed to ~ $\frac{104}{18} \approx 6$ for the lipids
↳ "give up fewer electrons" is fine

| Page | Score |
|---|---|
| 1 | /5 |
| 2 | /15 |
| 3 | /20 |
| 4 | /20 |
| 5 | /25 |
| 6 | /15 |
| Total | /100 |

Score for the page /15