

**Biochemistry 463, Summer II**  
**University of Maryland, College Park**  
**Biochemistry and Physiology**

Your Name: \_\_\_\_\_

Your SID #: \_\_\_\_\_

**Prof. Jason Kahn**

**Exam I (100 points total)**

**July 27, 2009**

You have 80 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. I have given you more space than you should need. There is extra space on the last page if you need it.

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.

Useful Equations:

$$\Delta S_{\text{system}} - \Delta H_{\text{system}}/T \geq 0$$

$$\text{pH} = -\log([\text{H}^+])$$

$$E = mc^2$$

$$S = k \ln W$$

$$\Delta G = \Delta H - T\Delta S$$

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$e^{i\pi} + 1 = 0$$

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. (35 pts) Amino acid structure and the peptide bond**

- (a; 8 pts) Draw the structure of arginine in its predominant ionic form at pH 7, including the stereochemistry at C $\alpha$ . Give its three-letter and one-letter codes. Give the name of the other amino acid that is positively charged at pH 7.

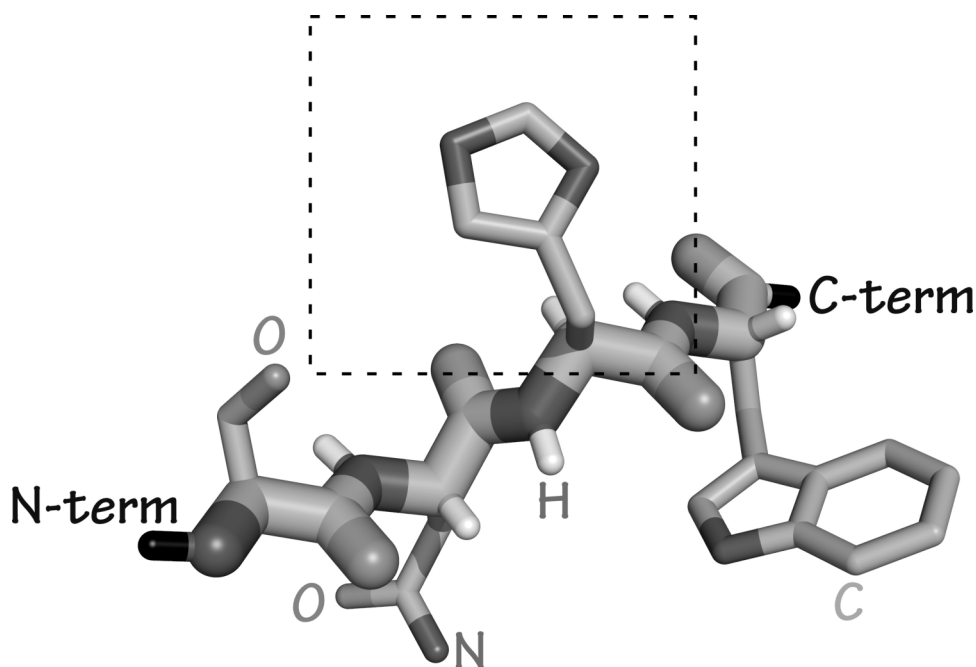
Score for the page \_\_\_\_\_

- (b; 4 pts) Why is it important to life that all amino acids in proteins have the same stereochemistry at  $C\alpha$ , as opposed to a random stereochemistry?

The diagram at the right shows a tetrapeptide. Each amino acid has the same pair of  $\Phi$  and  $\Psi$  angles. The backbone is thickened for your convenience. Side chain hydrogens are not shown.

- (c; 4 pts) Give the sequence of the peptide, using three-letter codes:

- (d; 3 pts) Fill in all the other hydrogens that one would find inside the dashed box at pH 4.



- (e; 4 pts) Indicate on the diagram one bond that defines a  $\Phi$  angle and one that defines  $\Psi$  (i.e. the bonds that one would look down to measure  $\Phi$  or  $\Psi$ ).

- (f; 3 pts) Circle the correct  $\Phi/\Psi$  pair:  $-120^\circ/120^\circ$      $0^\circ/180^\circ$      $-60^\circ/90^\circ$      $120^\circ/-60^\circ$

(g; 4 pts) Does this conformation look like it is in an allowed region of the Ramachandran plot? Why or why not?

(h; 5 pts) If this peptide conformation was part of a regular secondary structure, which one would it be and why?

**2. (40 pts) Protein Folding**

(a; 6 pts) Why are enzyme active sites typically formed at crevices on the surfaces of proteins rather than deep inside or on a convex surface, and why are active site residues typically not neighboring residues in regular secondary structures?

(b; 3 pts) What is the advantage of using the BLOSUM62 for BLAST searches, instead of just looking at whether amino acids in putative homologs are identical?

Part of the BLOSUM matrix from the text is shown below:

(c; 3 pts) Why is the score for replacing Cys with Cys higher than the score for Ala to Ala? (In other words, why is it more meaningful to find Cys in the same place in two potential homologs than it is to find Ala?)

(d; 3 pts) Why are there no replacements for Cys that contribute a positive score whereas there are several high-scoring replacements for Ile?

(e; 2 pts) Why is Val a better replacement for Ile even though Leu has the same molecular formula?

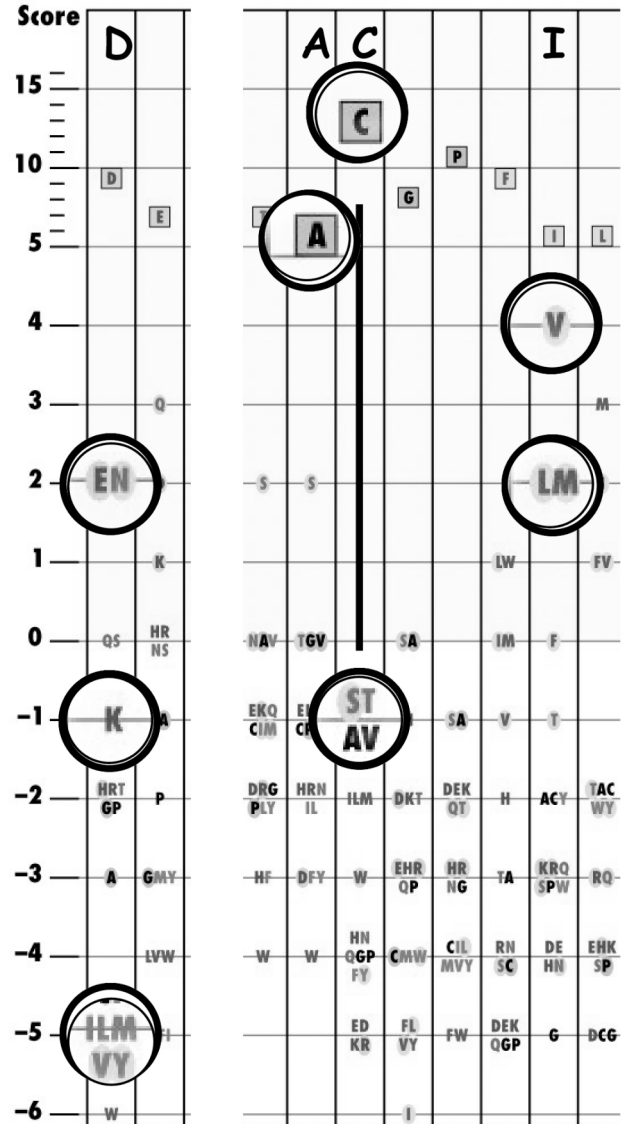


Figure 6-9  
Biochemistry, Sixth Edition  
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(f; 3 pts) Why is K, perhaps surprisingly, a more likely replacement for D than I, L, M, V, or Y?

The sketch below summarizes possible futures for the unfolded protein at the top left.

(g; 10 pts)

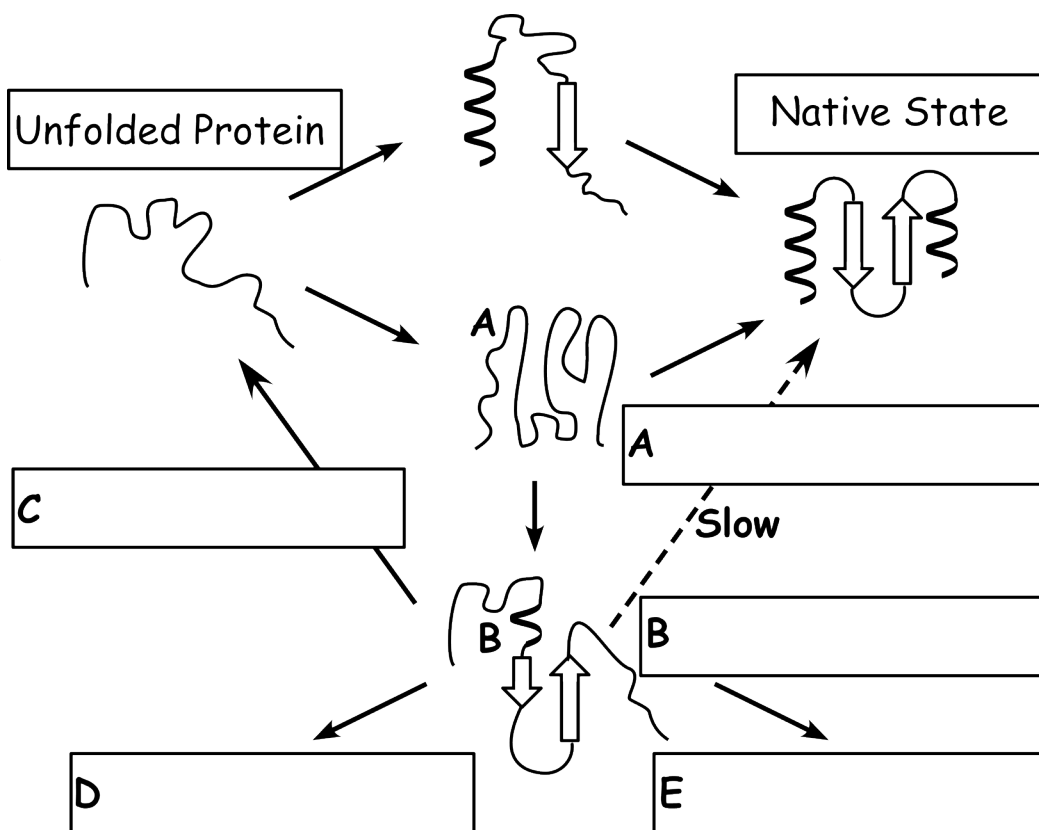
Identify on the sketch  
(write their names):

Possible folding  
intermediate (A)

State (B), which is  
analogous to a skier  
trapped at the  
bottom of a hill  
without a lift.

Protein or activity (C)  
that takes (B) back  
to Unfolded Protein

Two terminal fates (D)  
and (E)



(h; 3 pts) What particular feature of state (B) that differs from the native state targets state (B) to paths (C), (D), and/or (E)?

(i; 7 pts) How does the nanomachinery identified as (C) use the free energy of ATP hydrolysis to give proteins a second chance to fold?

**3. (25 pts) Biomolecules and Miscellaneous:**

(a; 3 pts) Give a redox-based explanation for why fat is a denser source of dietary calories than carbohydrates.

(b; 3 pts) Membranes undergo a transition from a liquid crystalline state to a more fluid state as the temperature increases. What does this simple observation tell us about the signs of  $\Delta H$  and  $\Delta S$  for forming the crystalline state?

(c; 3 pts) Bacteria make more *cis*-unsaturated fatty acids as the growth temperature decreases in order to increase membrane fluidity. Why do you think they make more saturated fatty acids as temperature goes up, i.e. what would be wrong with just using more *cis*-unsaturated fatty acids at all temperatures?

(d; 6 pts) We gave three main functions for carbohydrates in biology. List them and give an example of each.

(e; 5 pts) Draw the structure of  $\alpha$ -D-glucopyranose in the chair form.

(f; 5 pts) Calculate the ratio of  $[\text{ONO}^-]/[\text{HONO}]$  at pH 4.50 for nitrous acid, HONO,  $\text{p}K_a$  3.25.

(extra credit; 1 pt) What does TANSTAAFL stand for?

| Page         | Score       |
|--------------|-------------|
| 1            | /8          |
| 2            | /18         |
| 3            | /18         |
| 4            | /11         |
| 5            | /20         |
| 6            | /15         |
| 7            | /11         |
| <b>Total</b> | <b>/101</b> |

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