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#### **QUESTION 1**

Angular momentum is defined as:

- A. the dot product of position vector and linear momentum.
- B. the cross product of position vector and linear momentum.
- C. the simple product of position vector and linear momentum.
- D. the product of distance and linear momentum.

Correct Answer: B

#### **QUESTION 2**

Breast milk is proven to be the best form of nutrition for infants and is recommended for at least 1 year after birth. Unfortunately, a recent survey of breastfeeding mothers revealed that only 20% continue breastfeeding or to provide breast milk through pumping after 4 months, after which they switch to formula. When asked about reasons for stopping breastfeeding, the top three reasons were: going back to work, lack of support, and difficulties pumping. A socioeconomic study of the mothers revealed that women who choose to breastfeed for longest tend to have a higher level of education and come from more affluent backgrounds. Conversely, those mothers who breastfeed for the least amount of time tend to belong to minority groups and are from poorer backgrounds. It has been proposed that cultural differences also have a significant impact on the duration of breastfeeding.

Which statement would be supported by the knowledge that out of the women who took part in the socioeconomic survey, 2% were from a minority background?

- A. There are enough minority respondents to draw conclusions based on ethnicity.
- B. There are enough minority respondents to draw conclusions based on wealth.
- C. There are not enough minority respondents to make conclusions comparing ethnicity.
- D. There is no need to obtain more responses from minority groups.

Correct Answer: C

More responses from minority mothers are needed to make solid comparisons based on ethnicity.

#### **QUESTION 3**

Synthetic dyes constitute a commercially significant area of organic chemistry. The color producing properties of these compounds are the result of highly delocalized electron systems giving rise to electronic transitions whose absorptions occur in the visible region. Most commercially useful dyes can be classified as one of three types -- anthraquinones, azo dyes, or triarylmethyl salts. Examples of each type are illustrated in Figure 1.





# Figure 1

In order for a dye to be useful in the fabric industry, it must have sufficient affinity for the polymeric fibers of which the material is composed; the dye must not only impart a color to the fabric, but must also do so in a relatively permanent manner (color fastness). Proper design of synthetic polymers requires the placement of acidic or basic side chains along the polymer backbone such that binding sites are available for dying. Similarly, dyes must be produced not only with the appropriate color-producing structure, but also with an affinity for the fabric in question. The structural units of several common synthetic fibers are shown in Figure 2.





### Figure 2

Hydrogenation of alizarin over a specific rhodium catalyst results in the complete saturation of all the carbon-carbon bonds, but does not affect any other functional groups. Which of the following effects should also be expected?

A. The hydrogenated product will no longer have any affinity for Dacron fibers.

- B. The hydrogenated product will no longer be soluble in aqueous base.
- C. The hydrogenated product will no longer appear colored.
- D. The hydrogenated product will have a greatly increased affinity for nylon 610.

#### Correct Answer: C

As stated in the passage, color is the result of electronic transitions due to the delocalized system in the dye. If the two aromatic rings of alizarin are completely hydrogenated, the resulting compound will contain only the two isolated ketone double bonds; the system will thus no longer be delocalized, and color production will cease. Choice A is incorrect since the two H groups would still be present in the hydrogenated product; it is this feature of the molecule which accounts for the affinity for Dacron, via hydrogen bonding. Choice B is wrong since solubility in aqueous base is mainly due to the presence of the two H groups, and to a lesser extent to the polar carbonyl bonds, which will still be present in the hydrogenated product. Choice D is incorrect because it is not the aromatic nature of alizarin which accounts for its affinity, or lack thereof, for nylon 66. As the passage states, side chains are often necessary to provide a binding site; this is very likely to be the case between nylon and alizarin.

# **QUESTION 4**

Arginine is one of the 20 most common natural amino acids. Most healthy people do not need to supplement with arginine because the body usually produces sufficient quantities. The pathway for arginine synthesis was studied using



cells from a red bread mold. This natural form of arginine is illustrated below.



The red bread mold Neurospora crassa grows well on a cultural plate with "minimal" medium which is a fluid containing only a few simple sugars, inorganic salts, and vitamin. Neurospora that grows normally in nature (wild type) has enzymes that convert these simple substances into the amino acids necessary for growth. Mutating any one of the genes that makes an enzyme can produce a Neurospora strain that cannot grow on minimal medium. The mutant would only grow if the enzyme product were to be added as a supplement. On the other hand, if a "complete" medium is provided, containing all required amino acids, then Neurospora would grow, with or without mutation.



Figure 1 A synthesis pathway for the amino acid arginine. Each gene in italics in the diagram produces one enzyme necessary for the synthesis of this essential amino acid required for growth.

mutant strain	nothing	omithine	citrulline	argininosuccinate	arginine
P	-	-	-	+	+
Q		-	-	+	+



Table 1 Growth response of mutant strains in "minimal" media with supplements (ornithine, citrulline, argininosuccinate, and arginine) as indicated. Strain growth is indicated by (+) and no strain growth is indicated by (-). Which of the following is NOT an accurate description of naturally-occurring arginine?

- A. Acidic amino acid
- B. L-Configuration
- C. -Amino acid
- D. S-Configuration
- Correct Answer: A

The labeling of amino acids as acid, basic, hydrophilic, hydrophobic is based on the side chain. Two amino acids have acidic side chains at neutral pH. These are aspartic acid or aspartate (Asp) and glutamic acid or glutamate (Glu). Their side chains have carboxylic acid groups whose pKa\\'s are low enough to lose protons, becoming negatively charged.

Arginine and lysine are hydrophilic, basic amino acids. Their pKa\\'s are high enough that they tend to bind protons, gaining a positive charge (note that nitrogen can accept a proton). Histidine can act as an acid or base thus it is a good physiologic buffer.

Naturally occurring amino acids are -amino acids with the L-configuration (as opposed to most naturally occurring carbohydrates which are D-configuration).

The S-configuration can be confirmed by assigning priority at the carbon (i.e. carbon-2 which is the neighbor of the carbonyl C=O carbon): N > COOH > CC which is counterclockwise. Note that it is implied that the lowest group must be a hydrogen pointing away from the viewer since the dark triangle represents a group pointing out of the plane.

# **QUESTION 5**

Several models have been developed for relating changes in dissociation constants to changes in the tertiary and quaternary structures of oligomeric proteins. One model suggests that the protein\\'s subunits can exist in either of two distinct conformations, R and T. At equilibrium, there are few R conformation molecules: 10 000 T to 1 R and it is an important feature of the enzyme that this ratio does not change. The substrate is assumed to bind more tightly to the R form than to the T form, which means that binding of the substrate favors the transition from the T conformation to R.

The conformational transitions of the individual subunits are assumed to be tightly linked, so that if one subunit flips from T to R the others must do the same. The binding of the first molecule of substrate thus promotes the binding of the second and if substrate is added continuously, all of the enzyme will be in the R form and act on the substrate. Because the concerted transition of all of the subunits from T to R or back, preserves the overall symmetry of the protein, this model is called the symmetry model. The model further predicts that allosteric activating enzymes make the R conformation even more reactive with the substrate while allosteric inhibitors react with the T conformation so that most of the enzyme is held back in the T shape.

Experiment Evaluating Non-Symmetry Model Enzymes

Experiments were performed with enzyme conformers that did not obey the symmetry model. The data is summarized in Figure 1.



Figure 1: Equilibrium distribution of two conformers at different temperatures given the free energy of their interconversion. (modified from Mr.Holmium). All of the following statements are consistent with Figure 1 EXCEPT:

A. the products must have less free energy than the reactants in the exergonic reactions at the various temperatures.

B. the equation for the equilibrium constant K used to construct the graph is derived from  $G = -RT \ln K$ 

C. the 3 different temperature curves intersect at a point where the reaction is at equilibrium.

D. higher temperatures favor relatively more of the more stable conformer.

Correct Answer: D

Conformational isomers exist in a dynamic equilibrium, where the relative free energies of isomers determine the population of each isomer and the energy barrier of rotation determines the rate of interconversion between isomers.

Answer choice A: The graphs shows that for exergonic reactions (this means G

that the equilibrium constant K is defined as the product of the product concentrations divided by the product of reactant concentrations.

Answer choice B: divide both sides by -RT then raise both sides to the power of e. Remember from your rules of logarithms than e to the power of  $\ln x = x$ . Also recall that  $\ln is \log to the base e$ .

Answer choice C: From the graph, at a free energy difference of 0 kcal/mol (= equilibrium), this also gives an equilibrium constant of 1.

Answer choice D: A negative difference in free energy means that a conformer interconverts to a thermodynamically more stable conformation, thus the equilibrium constant will always be greater than 1. However, notice that K decreases with

increasing temperature meaning that there is more, relatively, of the less stable conformer (in other words, energy from the higher temperature is able to override the energy barrier to conversion to the less stable conformer). Thus the statement in answer choice D is incorrect which makes answer choice D the correct answer!



Going a bit further: notice that a positive difference in free energy means the conformer already is the more stable one, so the interconversion is an unfavorable equilibrium (K

equilibrium constant between two conformers can be increased by increasing temperature, meaning the amount of the less stable conformer present at equilibrium does increase slightly (see graph).

Note that: An endergonic process is accompanied by or requires the absorption of energy, the products being of greater free energy than the reactants. An exergonic process is the opposite and thus accompanied by the release of energy.

Incidentally, the enzyme subunits described in the passage exist in one of two conformations which stands for \\'tensed\\' (T) or \\'relaxed\\' (R), and as described relaxed subunits bind substrate more readily than those in the tense state. At any

rate, T/R was not to be considered in this question.

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