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Chemical Foundations

Review the Concepts

1. Less energy is required to form noncovalent bonds than covalent bonds, and the bonds that stick the gecko's feet to the smooth surface need to be formed and broken many times as the animal moves. Since van der Waals interactions are so weak, there must be many points of contact (a large surface area) yielding multiple van der Waals interactions between the septae and the smooth surface.
- 2a. These are likely to be hydrophilic amino acids, and in particular, negatively charged amino acids (aspartate and glutamate), which would have an affinity for K^+ via ionic bonds.
- 2b. Like the phospholipid bilayer itself, this portion of the protein is likely to be amphipathic, with hydrophobic amino acids in contact with the fatty acyl chains and hydrophilic amino acids in contact with the hydrophilic heads.
- 2c,d. Since both the cytosol and extracellular space are aqueous environments, hydrophilic amino acids would contact these fluids.
3. At $pH = 7.0$, the net charge is -1 because of the negative charge on the carboxyl residue of glutamate (E). After phosphorylation by a tyrosine kinase, two additional negative charges (because of attachment of phosphate residues to tyrosines (Y)) would be added. Thus, the net charge would be -3 . The most likely source of phosphate is ATP since the attachment of inorganic phosphate (P_i) to tyrosine is energetically highly unfavorable, but when coupled to the hydrolysis of the high-energy phosphoanhydride bond of ATP, the overall reaction is energetically favorable.
4. Disulfide bonds are formed between two cysteine residue side chains. The formation of disulfide bonds increases the order and therefore decreases the entropy (S becomes more negative).
5. Stereoisomers are compounds that have the same molecular formula but are mirror images of each other. Many organic molecules can exist as stereoisomers because of two different possible orientations around an asymmetric carbon atom (e.g. amino acids). Because stereoisomers differ in their three dimensional orientation and because biological molecules interact with one another based on precise molecular complementarity, stereoisomers often react with different molecules, or react differently with the same molecules. Therefore, they may have very distinct physiological effects in the cell.
6. The compound is guanosine triphosphate (GTP). Although the guanine base is found in both DNA and RNA, the sugar is a ribose sugar because of the 2' hydroxyl group. Therefore, GTP is a component of RNA only. GTP is an important intracellular signaling molecule.
7. At least three properties contribute to this structural diversity. First, monosaccharides can be joined to one another at any of several hydroxyl groups. Second, the C-1 linkage can have either an α or a β configuration. Third, extensive branching of carbohydrate chains is possible.
8. In the acidic pH of a lysosome, ammonia is converted to ammonium ion. Ammonium ion is unable to traverse the membrane because of its positive charge and is trapped within the lysosome. The accumulation of ammonium ion decreases the concentration of protons within lysosomes and therefore elevates lysosomal pH. At neutral pH, ammonia has little, if any, tendency to protonate to ammonium ion and thus has no effect on cytosolic pH.

$$9. \quad K_{\text{eq}} = [\text{LR}]/[\text{L}][\text{R}]$$

Since 90% of L binds R, the concentration of LR at equilibrium is $0.9(1 \times 10^{-3}\text{M}) = 9 \times 10^{-4}\text{M}$. The concentration of free L at equilibrium is the 10% of L that remains unbound, $1 \times 10^{-4}\text{M}$. The concentration of R at equilibrium is $(5 \times 10^{-2}\text{M}) - (9 \times 10^{-4}\text{M}) = 4.91 \times 10^{-2}\text{M}$. Therefore, $[\text{LR}]/[\text{L}][\text{R}] = 9 \times 10^{-4}\text{M} / ((1 \times 10^{-4}\text{M})(4.91 \times 10^{-2}\text{M})) = 183.3\text{M}^{-1}$.

The equilibrium constant is unaffected by the presence of an enzyme.

$$K_d = 1/K_{\text{eq}} = 5.4 \times 10^{-3}\text{M}.$$

10. The pH of cytosol is 7.2, which is the pK_a for the acid-base reaction, $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_2\text{PO}_4^{2-} + \text{H}^+$. Therefore, phosphoric acid will exist as a mixture of H_2PO_4^- and $\text{H}_2\text{PO}_4^{2-}$. Because the pK_a of phosphoric acid equals the optimal pH of cytosol, phosphoric acid serves as a biological buffer to help the cell maintain a constant pH.

$$11. \quad \Delta G = \Delta G^\circ + RT \ln [\text{products}]/[\text{reactants}]$$

For this reaction, $\Delta G = -1000\text{ cal/mol} + [1.987\text{ cal}/(\text{degree}\cdot\text{mol}) \times (298\text{ degrees}) \times \ln (0.01\text{ M} / (0.01\text{ M} \times 0.01\text{ M}))]$.

$$\Delta G = -1000\text{ cal/mol} + 2727\text{ cal/mol} = 1727\text{ cal/mol}$$

To make this reaction energetically favorable, one could increase the concentration of reactants relative to products such that the term $RT \ln [\text{products}]/[\text{reactants}]$ becomes smaller than 1000 cal/mol. One might also couple this reaction to an energetically favorable reaction.

12. The presence of one or more carbon-carbon double bonds is indicative of an unsaturated or polyunsaturated fatty acid. The term *saturated* refers to the fact that all carbons, except the carbonyl carbon, have four single bonds. In a cis unsaturated fatty acid the carbon atoms flanking the double bond are on the same side, thus introducing a kink in the otherwise flexible

straight chain. There is no such kink in a trans unsaturated fatty acyl chain.

13. Glutamate is the amino acid that undergoes γ -carboxylation, resulting in the formation of a host of blood clotting factors. Warfarin inhibits γ -carboxylation of glutamate. Thus, blood clotting is severely compromised. Patients prone to forming clots (thrombi) in blood vessels might be prescribed warfarin in order to prevent an embolism, which would result if the clot dislodged and blocked another vessel elsewhere in the body). Patients at risk for heart disease due to blockages in the coronary arteries are also often prescribed this drug.