# CHAPTER - 2

- **1.** pH 1.1.
- For the equilibrium HA → H<sup>+</sup> + A<sup>-</sup>, the corresponding Henderson-Hasselbalch equation is : pH = pK<sub>a</sub> + log [A<sup>-</sup>]/[HA]. When the acid is half-ionized, [HA] = [A<sup>-</sup>]. Hence [A<sup>-</sup>]/[HA] = 1; log 1 = 0; and pK<sub>a</sub> = pH.
- **3.** (a) In a zone centred about pH 9.6 (b) 4/5 (c)  $10^{-2}$  L (d) pH pK<sub>a</sub> = -2
- 4. (d); the weak base bicarbonate will titrate OH to  $-O^-$ , making the compound more polar and more water-soluble.
- 5. Stomach; the neutral form of aspirin present at low pH is less polar, and therefore more membrane permeant.
- 6. Surface tension of water is so strong that it does not allow water to form stable bubbles when blown through a pipe. Soaps and detergents contain a basic cleaning agent called surfactant or surface active agent. *Surfactants lower the surface tension of water sufficiently to enable a film of soap solution to be blown as bubbles.* So soapy water is used by children to blow bubbles.
- 7. A pure liquid such as water freezes completely at a constant temperature which is known as the freezing point for that liquid. But the addition of any soluble impurity lowers the freezing point of the mixture so formed. When salt is sprinkled on ice, a part of it dissolves in the water film that always covers the ice surface. As the freezing point of the solution so formed is much lower than the freezing point of water, it remains in a liquid state and continues dissolving more salt and melting more ice. This phenomenon is used to clear snow from roads and side-walks in cold countries during winter.
- 8. Water is a polar solvent, that is, its molecules behave like dipoles with two oppositelycharged ends. Common salt is a crystalline substance made up of sodium (Na<sup>+</sup>) and chloride (Cl<sup>-</sup>) ions, held together by strong electrostatic forces. When salt is put in water, the water molecules get attached to the sodium and chloride ions and neutralize the force of attraction between them. The negatively-charged chloride ions get surrounded by the positive ends of the water molecules, while the positively-charged sodium ions get surrounded by the negative ends of the water molecules. As a result, water molecules tend to pull the ions away from the solid crystal lattice, making salt dissolve in water. Oil, on the other hand, is not a polar solvent and its molecules are not able to neutralize

the electrostatic force of attraction between ions. Salt, therefore, does not dissolve in oil.

**9.** Paper is made up of thin sheets of cellulosic fibres and other ingredients mixed together. It is sized to make it suitable for writing. The cellulosic fibres are held together by weak forces called the van der Waal's forces. When paper is dipped in water, the sizing material used for refining the paper being water-soluble becomes soft. Water being a polar solvent, weakens the van der Waal's forces that hold the fibres together. As a result, the fibres come off easily when pulled and so a wet paper tears off easily. On the other hand, oil being a nonpolar solvent does not affect the water-soluble sizing material. Nor does it weaken the forces holding the cellulosic fibres together. So paper soaked in oil does not tear off as easily as paper soaked in water does.

- 10. The surface of water behaves like any stretched membrane. In other words, when it is ruptured at any point it shrinks away. This property is known as surface tension. Some substances such as oil, grease or detergents have the property of reducing the surface tension when added to water. When we touch a wet surface with our fingertips, the oil on our fingertips which is always present on the unwashed finger reduces the surface tension of water at that point and the water film moves away. The area of the surface from which the water film moves away depends on how oily the finger is.
- 11. Wetting is a phenomenon which depends to a large extent on the difference between the adhesive force between a liquid and the surface in contact and the cohesive force between the molecules of the liquid which is also a measure of its surface tension. Mercury does not wet the surface of glass because of its higher surface tension which is six times that of water. In case of mercury, the cohesive force is much stronger than the adhesive force, that is the force of attraction between molecules of mercury and of glass. As a result, mercury neither spreads out nor wets the surface of glass is stronger than the cohesive force between water and glass is stronger than the cohesive force between water molecules which makes water to spread out and cling to the surface of glass wetting it.
- 12. Ice is nothing but solidified water in which  $H_2O$  molecules are bound together by the weak hydrogen bonds and form an open cage-like structure. When ice is subjected to pressure, the hydrogen bonds being the weaker ones break easily. Consequently, the  $H_2O$  molecules get separated and ice melts into water. Whereas in the case of paraffin wax, which is hydrocarbon petroleum product, carbon atoms are held together by covalent bond. Also, since it is plastic solid, it usually deforms under pressure without the application of heat. When pressure is applied on soft wax, the molecular spaces decrease and molecules tend to come closer, thereby causing hardening of wax.
- 13. Ice cubes are preferred to water at 0°C to cool a soft drink because when ice melts, it absorbs a certain amount of heat known as latent heat until it is melted. *The heat absorbed does not raise the temperature of the drink but goes entirely into changing the ice into water. Thus ice cubes added to a drink chill it by absorbing heat from it.* On the other hand, chilled water at 0°C simply mixes up with the drink and the temperature attained by the mix will only be an average of the temperatures of the two. Hence, ice cubes are preferred over chilled water for cooling a soft drink.
- 14. Whenever a solute is dissolved in water, some energy change takes place. In most cases, the amount of this change is very small and is hardly noticeable. But in some cases, it is quite large and leads to large changes in temperature a rise or fall depending upon whether the heat of solution is positive or negative. *Glucose has a negative heat of solution, i.e., heat is absorbed when glucose is dissolved in water. As a result, the temperature drops and the solution feels cool.*
- **15.** Although hydrogen is a combustible gas and oxygen a supporter of combustion, when combined to form water they lose their individual properties. Water is not a mixture but a compound formed by the chemical reaction between hydrogen and oxygen in a definite proportion. Since the properties of a compound are entirely different from the properties of its constituent elements, water does not burn or support combustion. Rather because of its high heat capacity, it is an excellent coolant and fire-extinguisher.
- 16. Both snow and foam look white due to the same reason. While foam is a collection of large number of bubbles, snow is made up of large number of ice-crystals. In both snow and foam, the gaps between the bubbles or the crystals is filled by air. Light rays falling on such a collection of crystals gets bent and reflected by the crystals. However, all the crystals do not reflect or refract the light in the same direction. Thus, light gets scattered

haphazardly. The presence of air adds to this scattering. The light reaching an observer looking at the snow, therefore, is just the scattered light and so the snow looks white. In case of water, the situation is different. Here since the water surface is smooth, very little light gets scattered although a part of it is reflected. Almost all of the light falling on a clear water surface passes through it to the other side making water look transparent.

- 17. Oxygen and sulphur belong to the same group in the periodic table, so theoretically the hydrides of these elements should have very similar properties. But in reality, there is a large difference in the physical properties of these hydrides. For example, water is a liquid and hydrogen sulphide is a gas. This unusual behaviour of water arises from its unique property of forming weak bonds called hydrogen bonds. In water, large number of  $H_2O$  molecules are held together by these bonds which form between O and H, thus effectively forming a giant molecule. As is the rule, with the increase in the molecular weight, the boiling point of water rises, compared to what it should be, had there been no hydrogen bonding, and it remains a liquid at room temperature. This does not happen with hydrogen sulphide and so it remains a gas.
- 18. Sea water is salty because it contains many dissolved salts, mostly sodium chloride with small proportions of potassium, magnesium, calcium and carbonates. The salt comes mainly with river water that flows through rocks eroded by frost and rain. The gradual wearing away of mountains releases chemicals which are carried down by rivers to the ocean as dissolved salts. Some salt also enters seawater from the rocks beneath the seabed. The river water carrying the salts to the sea does not taste salty because the salts are present in extremely small concentration. Whereas in the case of the oceans, water is continuously evaporating even as more and more salt continues to be added with river water. This, over millions of years has led to the high concentration of dissolved salts in seawater.
- **19.** Lakes that appear frozen from the top never freeze completely. Only the top layer freezes and a thick layer of ice floats on water which remains liquid below and in which fishes and other aquatic animals survive. With the onset of winter, water starts cooling. As it cools, it shrinks in volume and becomes denser, but only until it reaches 4°C. Below that temperature, water expands and its density drops. This comparatively lighter water moves up and finally at 0°C it turns into ice. Since the density of ice is less than that of water, the ice floats. Also, ice being a very poor conductor of heat, further cooling of the water below it stops. Thus, the temperature of water below the ice layer remains at 4°C and fishes survive in it.
- **20.** About 60 per cent of our body weight is water. Water is constantly lost from our body through exhalation, perspiration and urine. At the same time, we obtain a good amount of water from our food, but it is not enough to keep the balance of water our body needs. That is why we need to drink water from time to time. When the water balance is disturbed, either due to excessive loss by perspiration or due to insufficient intake, the salt content of the blood changes. This change activates the thirst centre in our brain which makes us feel thirsty
- **21.** Water supplied to cities and towns is usually taken from rivers or lakes and contains various kinds of pollutants, and so it has to be purified. First, the raw water is passed through screens to separate coarse solids and it is then fed into settling tanks where the suspended solids settle out. Sometimes, substances such as alum are added to aid the settling process. From the settling tanks the water is sent to sand filter beds, which are large concrete tanks with thick layers of coarse and fine sand at the bottom. The sand filters remove the remaining suspended matter from the water. Finally, the clear water is treated with chlorine gas in a closed tank to kill bacteria. The purified water is then

pumped into tanks for distribution. For industrial use, water is sometimes passed through ion exchangers to remove ions like magnesium and calcium present in hard water.

#### **CHAPTER - 3**

- **1.** (*a*) pH = 0.456.
  - (b) pH = 2.608 by approximation, 2.609 exact.
  - (c) pH = 3.108 by approximation, 3.113 exact.
- **2.** (*a*) pH = 4.46.
  - (*b*) pH = 2.57.
- 3. The best choice would be a mixture of  $H_2PO_4^-$  and  $HPO_4^{2-}$ , which has  $pK_a = 6.86$ .
- **4.** Because of the proton-attracting power of the dianion produced when two of the citric acid protons have dissociated, the third is held anomalously strongly. In fact, it has a  $pK_a$  of 6.86.
- 5. If a weak acid is 91% neutralized, 91 parts are present as conjugate base and 9 parts remain as the undissociated acid. Thus, the conjugate base/acid ratio is approximately 10:1. Substituting this ratio into the Henderson–Hasselbalch equation gives  $5.7 = pK' + \log (10/1)$ . Solving the equation for pK' gives an answer of 4.7. The acid could be  $\beta$ -hydroxybutyric acid, an important physiological acid, which has this pK'.
- 6. One need to simply substitute the given values into the Henderson–Hasselbalch equation:

$$7.45 = 6.1 + \log (x/1.25)$$

$$1.35 = \log(x/1.25)$$

The antilog of 1.35 is 22.39. Therefore

 $[HCO_3^-] = 22.39 \times 1.25 = 27.98 \text{ mM}$ 

- Normal  $[HCO_3^-] = 24.0 \text{ mM}$  so there is an increase of 3.98 mmol (per liter) of  $HCO_3^-$ .
- 7. Physical properties of a compound, such as colour, taste, touch etc, depend on its pH factor. The pH further depends upon the concentration of H<sup>+</sup> and OH<sup>-</sup> ions in that compound. For example, compounds having higher concentration of H<sup>+</sup> ions are sour like acids and compounds having higher OH<sup>-</sup> ion concentration are bitter like bases. Water has an equal concentration of H<sup>+</sup> and OH<sup>-</sup> ions. Thus, it has neither sour nor a bitter taste and hence it is tasteless. Similarly, it is colourless and does not have an odour.

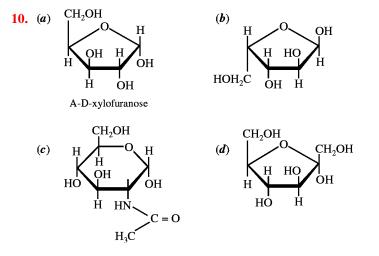
## **CHAPTER - 4**

1.  $CCl_4$ ,  $H_2S$ ,  $H_3N - CH_2 - COO^-$ ,  $-H_3N - CH_2 - CH_2 - CH_2 - COO^-$ .  $CCl_4$  is symmetrical,  $\mu = 0$ ;  $H_2S$  will be comparable to  $H_2O$ ; the latter two involve separation of whole charges, and in the last, separation is greatest.

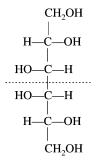
- **1.** Carbohydrates were originally regarded as *hydrates* of *carbon* because the empirical formula of many of them is  $(CH_2O)_n$ .
- **2.** (a) aldose-ketose; (b) epimers; (c) aldose-ketose; (d) anomers; (e) aldose-ketose; (f) epimers.

- **3.** Aldoses are converted into aldonic acids; the aldehyde group of the sugar is oxidized to a carboxylate.
- 4. The proportion of the  $\alpha$ -anomer is 0.36, and that of the  $\beta$ -anomer is 0.64.
- 5. Glucose is reactive because of the presence of an aldehyde group in its open-chain form. The aldehyde group slowly condenses with amino groups to form Schiff-base adducts.
- 6. A pyranoside reacts with two molecules of periodate; formate is one of the products. A furanoside reacts with only one molecule of periodate; formate is not formed.
- 7. From methanol.
- **8.** Heating converts the very sweet pyranose form to the more stable but less sweet furanose form. Consequently, it is difficult to accurately control the sweetness of the preparation, which also accounts for why honey loses sweetness with time.
- 9. (a) Each glycogen molecule has one reducing end, whereas the number of nonreducing ends is determined by the number of branches, or  $\alpha$ -1,6 linkages.

(b) Because the number of nonreducing ends greatly exceeds the number of reducing ends in a collection of glycogen molecules, all of the degradation and synthesis of glycogen takes place at the nonreducing ends, thus maximizing the rate of degradation and synthesis.

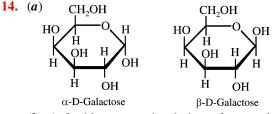


**11.** Galactitol has the following structure:



Since it has a plane of symmetry between C-3 and C-4, it is optically inactive. Such compounds, which contain asymmetric carbons but have no net optical activity, are called *meso* forms.

- 12. In the chair form, there is more steric clash between the 2-OH and the 1-OH in the  $\alpha$  form of glucose and in the  $\beta$  form of mannose (compare glucose and mannose). Furthermore, dipole–dipole interactions will be more favourable in  $\beta$ -D-glucose and  $\alpha$ -D-mannose.
- **13.** Hyaluronic acid.



(b) A freshly prepared solution of  $\alpha$ -D-galactose undergoes mutaroation to yield an equilibrium mixure of  $\alpha$ - and  $\beta$ -D-galactose. Mutarotation of either the pure  $\alpha$  or the pure  $\beta$  form will yield the same equilibrium mixture.

(c) 72%  $\beta$  form; 28%  $\alpha$  form.

**15.** Yes; the empirical formula is CH<sub>2</sub>O, typical of a carbohydrate.

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CHAPTER - 6
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- 1. Glucose is reactive because its open-chain form contains an aldehyde group.
- **2.** (*d*) glucose

# CHAPTER - 7

1. (a) Measure the change in optical rotation with time.

(b) The optical rotation of the mixture is negative (inverted) relative to that of the sucrose solution.

(c) 0.63.

- **2.** Prepare a slurry of sucrose and water for the core; add a small amount of invertase; immediately coat with chocolate.
- 3. Sucrose is not a reducing sugar.
- **4.** Lactose; in sucrose, the anomeric carbons of both glucose and fructose are involved in the glycosidic bond and are not available to reduce Fehling's reagent. Lactose is a reducing sugar that converts Fe<sup>3+</sup> to Fe<sup>2+</sup>, which precipitates as the red oxide.
- 5. Oligosaccharides; their subunits can be combined in more ways than the amino acid subunits of oligopeptides. Each of the several hydroxyl groups can participate in glycosidic bonds, and the configuration of each glycosidic bond may be either  $\alpha$  or  $\beta$ . Furthermore, the polymer may be linear or branched.

- 1. As an unbranched polymer,  $\alpha$ -amylose has only one nonreducing end. Therefore, only one glycogen phosphorylase molecule could degrade each  $\alpha$ -amylose molecule. Because glycogen is highly branched, there are many nonreducing ends per molecule. Consequently, many phosphorylase molecules can release many glucose molecules per glycogen molecule.
- 2. 7,840 residues/s.
- **3.** The human intestinal enzyme that splits  $(1 \rightarrow 4)$  linkages between glucose residues is

absolutely specific for the  $(\alpha 1 \rightarrow 4)$  linkage; cellulose, with its  $(\beta 1 \rightarrow 4)$  linkages, cannot be digested.

4. Native cellulose consists of glucose units linked by  $(\beta 1 \rightarrow 4)$  glycosidic bonds. The  $\beta$  linkage forces the polymer chain into an extended conformation. A parallel series of these extended chains can form intermolecular hydrogen bonds, aggregating into long, tough, insoluble fibres. Glycogen consists of glucose units linked together by  $(\alpha 1 \rightarrow 4)$  glycosidic bonds. The  $\alpha$  linkage causes a bend in the chain and prevents the formation of long fibres. In addition, glycogen is highly branched. Because many of its hydroxyl groups are exposed to water, glycogen is highly hydrated, and can be extracted as a dispersion in hot water.

The physical properties of these two polymers are well suited for their biological roles. Cellulose serves as a structural material in plants, consistent wih its side-by-side aggregation into insoluble fibres. Glycogen serves as a storage fuel in animals. The highly hydrated glycogen granules with their abundance of nonreducing ends can be rapidly hydrolyzed by glycogen phosphorylase to release glucose-1-phosphate.

- 5. Chains of  $(1\rightarrow 6)$ -linked D-glucose residues with occasional  $(1\rightarrow 3)$ -linked branches, with about one branch for every 20 residues in the polymer.
- 6. The negative charges on chondroitin sulfate repel each other and force the molecule into an extended conformation. Furthermore, the polar structure attracts many water molecules (water of hydration), which increases the molecular volume of the chondroitin sulfate.
- 7. Writing with ink on a surface depends on both the ink and the surface. Ink contains a colouring substance (dye) dissolved in water or a volatile solvent. As paper is made of cellulose, when we write with a fountain pen, the colouring substance in the ink enters the fine capillaries through capillary action. When the solvent evaporates, dry ink remains in the capillaries, thus making the visible mark on the paper. If the surface of the paper is oily, the oil repels the ink which as a result does not stick to the paper to produce a mark. So, it is not possible to write on oily paper with a fountain pen.

On the other hand, a ball-point pen does not write on oily paper for a different reason. When drawn over the oily surface, the ball on the tip of a ball-point pen slips and does not rotate as there is no friction. As a result, the thick ink does not flow out and does not write.

- 8. Apples contain tannins which act as *astringent agents i.e., is they demoisturise the fruit.* Their concentration in the apple depends upon the season and the stage of maturity of the fruit. When the apple is green, the concentration of tannins is high and it decreases as the fruit matures. When the apple is sliced or cut, tannins get exposed to the air. In presence of some enzymes that apples contain, tannins combine with oxygen in the air to form oxides which impart an orangish hue to the sliced part.
- **9.** Gun cotton is a highly inflammable, explosive chemical called cellulose nitrate. If is prepared by treating cotton, a natural almost pure (94%) cellulose, with concentrated nitric acid and hence the name gun cotton. Due to its inflammable nature and with the arrival of better plastic material, its use has been discontinued. However, it is still used for making certain kinds of explosives.
- **10.** In the form of starch in plants and in the form of glycogen in animals.
- **11.** No, any starch will increase one's blood sugar some. One should always eat a well-balanced diet that includes various starches.
- **12.** Because starch molecule is highly hydrated since it contains many exposed hydroxyl groups.
- **13.** Paper is made of cellulose fibres found in plant cell walls. The fibres are beaten into pulp and joined together by the action of water to form sheets of paper. It is these fibres which

break when we try to tear a sheet of paper. As these fibres are randomly placed with respect to each other, they can break in any direction when one pulls a paper apart. However, when we fold a paper, the fibres get uniformly weakened along a straight line. So, when this folded paper is pulled apart to tear it, those weakened fibres give way easily and the paper gets torn along the straight line.

14. Paper is made of cellulose fibres and other ingredients mixed together. The smooth surface of finished paper results from the process of paper making itself. During manufacture, the wet film of pulp is drained, dried and finally calendered by pressing it between steam-heated rollers which set the fibres in place in a somewhat stretched condition. When paper is dipped in water, the sizing material gets loosened, the fibres soak water and get deformed. If this wet paper is allowed to dry, it gets wrinkled because the fibres dry in a deformed state.

## CHAPTER - 9

1. (a) Each strand is 35 kd and hence has about 318 residues (the mean residue mass is 110 daltons). Because the rise per residue in an  $\alpha$  helix is 1.5 Å, the length is 477 Å. More precisely, for an  $\alpha$ -helical coiled coil the rise per residue is 1.46 Å so that the length will be 464 Å.

(b) Eighteen residue in each strand (40 minus 4 divided by 2) are in a  $\beta$ -sheet conformation. Because the rise per residue is 3.5 Å, the length is 63 Å.

- 2. Glycine has the smallest side chain of any amino acid. Its size often is critical in allowing polypeptide chains to make tight turns or to approach one another closely.
- **3.** Glutamate, aspartate, and the terminal carboxylate can form salt bridges with the guanidinium group of arginine. In addition, this group can be a hydrogen-bond donor to the side chains of glutamine, asparagine, serine, threonine, aspartate, and glutamate, and to the main-chain carbonyl group.
- 4. Disulfide bonds in hair are broken by adding a thiol and applying gentle heat. The hair is curled, and an oxidizing agent is added to re-form disulfide bonds to stabilize the desired shape.
- **5.** The energy barrier that must be crossed to go from the polymerized state to the hydrolyzed state is large even though the reaction is thermodynamically favourable.
- 6. Using the Henderson-Hasselbach equation, we find the ratio of alanine-COOH to alanine-COO<sup>-</sup> at pH 7 to be  $10^{-4}$ . The ratio of alanine-NH<sub>2</sub> to alanine-NH<sub>3</sub><sup>+</sup>, determined in the same fashion, is  $10^{-1}$ . Thus, the ratio of neutral alanine to zwitterionic species is  $10^{-4} \times 10^{-1} = 10^{-5}$ .
- 7. The assignment of absolute configuration requires the assignment of priorities to the four groups connected to a tetrahedral carbon. For all amino acids except cysteine, the priorities are: (1) amino group; (2) carbonyl group; (3) side chain; (4) hydrogen. For cysteine, because of the sulfur atom in its side chain, the side chain has a greater priority than does the carbonyl group, leading to the assignment of an R rather than S configuration.
- **8.** LEARNINGSCIE(N)CEISGREAT.
- 9. No, Pro-X would have the characteristics of any other peptide bond. The steric hindrance in X-Pro arises because the R group of Pro is bonded to the amino group. Hence, in X-Pro, the proline R group is near the R group of X. This would not be the case in Pro-X.
- 10. Treatment with urea will disrupt noncovalent bonds. Thus, the original 60-kd protein must

be made of two 30-kd subunits. When these subunits are treated with urea and mercaptoethanol, a single 15-kd species results, suggesting that disulfide bonds link the 30-kd subunits.

- Because three-dimensional structure is much more closely associated with function than is sequence, tertiary structure is more evolutionarily conserved than is primary structure. In other words, protein function is the most important characteristic, and protein function is determined by structure. Thus, the structure must be conserved, but not necessarily a specific amino acid sequence.
- 12. Protein A is clearly homologous to protein B, given 65% sequence identity, and so A and B are expected to have quite similar three-dimensional structures. Likewise, proteins B and C are clearly homologous, given 55% sequence identity, and so B and C are expected to have quite similar three-dimensional structures. Thus, one can conclude that proteins A and C are likely to have similar three-dimensional structures, even though they are only 15% identical in sequence.
- 13. In a hydrophobic environment, the formation of intrachain hydrogen bonds would stabilize the amide hydrogen atom and carbonyl oxygen atoms of the polypeptide chain; so an  $\alpha$  helix would form. In an aqueous environment, these groups would be stabilized by interaction with water, so there would be no energetic reason to form an  $\alpha$  helix. Thus, the  $\alpha$  helix would be most likely to form in an hydrophobic environment
- **14.** 109.5.
- 15. (a) SYSMEHFRWGKPV.

(b) 1624. This is not exactly correct because it does not take into account dissociation of some protons.

- **16.** AC.
- **17.** (*a*) 2.

(b) Between the first and second, and third and fourth cysteines.

- 18. They are spaced about three to four residues apart. Therefore, they will all lie on the same side of the  $\alpha$  helix. This suggests that this side of the helix may face the interior of the protein.
- **19.** (a)  $3^{200} = 2.7 \times 10^{95}$ .

(b) Not all of these conformations will be sterically possible. But even if only 0.1% of these are allowed, there are still  $2.7 \times 10^{92}$ , a very large number.

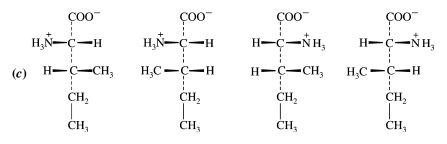
- 20. Assuming that x-ray diffraction is not practical, we have:
  - (a) Analysis by CD or by NMR.
  - (**b**) Sedimentation equilibrium.

(c) More than one secondary/tertiary folding can be observed for the same sequence. Therefore, sequence alone cannot dicate folding in all cases, and sequence-based predictions must sometimes fail badly.

- **21.** Chloride ions must interact with positively charged groups so as to stabilize the deoxy state. Thus, the higher the Cl<sup>-</sup> concentration, the lower the  $O_2$  affinity of hemoglobin will be.
- 22. L; determine the absolute configuration of the  $\alpha$  carbon and compare with D- and L-glyceraldehyde.
- **23.** (*a*) 2
  - **(b)** 4

## Contents

#### **1172** FUNDAMENTALS OF BIOCHEMISTRY



- **24.** 1,220; 12,200
- **25.** 75,020
- 26. Carboxyl groups; Asp and Glu
- **27.** (a)  $(\text{Glu})_{20}$  (b)  $(\text{Lys-Ala})_3$  (c)  $(\text{Asn-Ser-His})_5$  (d)  $(\text{Asn-Ser-His})_5$
- **28.** The principal structural units in the wool fibre polypeptides are successive turns of the  $\alpha$  helix, which are spaced at 0.54 nm intervals. Steaming and stretching the fibre yields an extended polypeptide chain with the  $\beta$  conformation, in which the distances between the R groups are about 0.70 nm. On shrinking, the fibre reassumes an  $\alpha$ -helical structure.
- **29.** The disulfide bonds are covalent bonds, which are much stronger than the noncovalent bonds that stabilize most proteins. They serve to cross-link protein chains, increasing their stiffness, mechanical strength, and hardness.
- 30. Wool shrinks when polypeptide chains are converted from the extended conformation (β-pleated sheet) to the α-helical conformation in the presence of heat. The β-pleated sheets of silk, with their small, closely packed amino acid side chains, are more stable than those of wool.
- **31.** At residues 7 and 19; prolines are often but not always found at bends. Between residues 13 and 24.
- **32.** Myoglobin is a monomer with one globin and one heme binding one  $O_2$ .  $O_2$  binding is a simple equilibrium with a Hill coefficient of 1. Hemoglobin is a tetramer with four  $O_2$  bound to the four hemes. Hemoglobin without oxygen is in the T conformation in which binding of  $O_2$  is difficult. Thus, the curve starts with a slow increase as  $pO_2$  increases. Binding of the first  $O_2$  shifts the conformation of the whole molecule to favour the R form, which binds  $O_2$  more readily. Thus, the slope rises steeply giving it a sigmoidal shape. This is an example of cooperativity. The Hill coefficient for hemoglobin is 2.8.
- 33. Trypsin cleavage gives (a) His-Ser-Lys + (b) Ala-Trp-Ile-Met-Cys-Gly-Pro-Arg + (c) His-His-Ala. Further degradation of (a) is accomplished by elastase and dipeptidase. Further degradation of (b) would start with chymotrypsin and also use dipeptidases, tripeptidase, and carboxypeptidase B. To degrade (c), carboxypeptidase A and dipeptidase would be enough. The point is that several peptidases with varying specificities are required.

His-Ser-Lys-Ala-Trp-Ile-Asp-Cys-Pro-Arg-His-His-Ala

- **34.** Methods of removal of hair are classified as *depilatory* (removal of hair from the surface of the skin) or *epilatory* (removal of intact hair with the root). Depilatory creams are substituted mercaptans, such as thioglycollic acid, which reduce the disulfide bond in the peptide chains of keratin, a hair protein. As a result, the hair fibre swells and softens and can be washed from the skin.
- **35.** (*a*) Both myoglobin and hemoglobin
  - (b) Both myoglobin and hemoglobin
  - (c) Hemoglobin

- (d) Myoglobin
- (e) Neither of the two
- (f) Both myoglobin and hemoglobin
- (g) Hemoglobin
- (h) Both myoglobin and hemoglobin
- (i) Hemoglobin
- (j) Neither of the two
- **36.** Homocysteine is a normal building block for protein, and too much can damage one's arteries. Vitamins  $B_6$ ,  $B_9$  and  $B_{12}$  can lower it.
- **37.** Scalp hair is not the same among all the people in the world. The Negro has tightly curled hair while the American Indians have straight, lank and coarse hair. The Caucasians have hair that may be straight or wavy or curly. Australian natives have "frizzly" hair. So the type of hair one has depends on one's racial inheritance and is genetically determined. *The reason why someone's hair is curly while another's is not depends on the structure of the strand of hair.* If you cut a shaft of hair transversely and observe it under microscope, the difference would become clear. *The cut section of curly hair is flat.* The flatter the hair, the more easily it bends and hence the curlier it becomes. *Straight hair has a round cross-section.* Thus what kind of hair you have would be genetically determined and stable for a life-time. Cosmetic treatment can only temporarily curl or straighten hair as per our wishes.
- **38.** Wrinkling of skin is a sign of old age. Our skin becomes wrinkled because of changes in the underlying structure. There are some connective tissues just under the outer layer of the skin which are made up of two types of protein fibres—collagen and elastin. The collagen provides the material for the tissue and the elastin fibres, which are smaller in number, give elasticity and suppleness to the skin. *With time, as one ages, the amount of elastin in the skin diminishes and the collagen fibres become disorganized. The cross-linking between collagen fibres also increases. Consequently, the tissue gradually loses its elasticity. Thus, wrinkles appear on the face and other parts of the body. Another factor responsible for the development of wrinkles is sunlight. <i>The ultraviolet part of the sunlight accelerates the changes in the skin which cause wrinkles.*
- **39.** Homocysteine is a substance made in the body. Too much of it means one has an increased risk of heart attack and stroke.
- **40.** A deep wound or cut usually leaves a scar whereas a superficial one seldom does so. A wound in which collage fibres situated deep in the dermis layer of the skin are damaged leaves a scar. This is because the collagen fibres are arranged in the skin in a specific sequencial manner. To restore the same sequence when wound is healing is not possible. As a result of a change in the deposition pattern of collagen fibres, a scar is formed on the skin.
- **41.** Pain is felt only when a nerve end is stimulated by a cut or injury. Since hair and nails do not have nerve endings, cutting them does not produce pain. However, cells at the base of a nail and hair are living cells and have nerve endings. So, if a nail is cut from the base or if a hair is plucked off, pain is felt.

# **CHAPTER - 11**

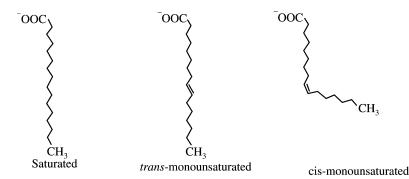
1. You must have the correct N- and C-terminal amino acids and the correct total number (12) of amino acids in the peptide. Keeping these criteria in mind and overlapping the

fragments, you should get the sequence: Met-Phe-Pro-Met-Gly-Leu-Arg-Lys-Glu-Ala-Ala-Ile. Note that the Lys-Glu fragment doesn't give any additional information for the sequencing.

2. Pepsin partially digests (hydrolyzes) the protein in foods.

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CHAPTER - 12
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1. The presence of a *cis* double bond introduces a kink that prevents packing of the fatty acid chains. *Cis* double bonds maintain fluidity. *Trans* fatty acids have no structural effect, relative to saturated fatty acids, and so they are rare.



- 2. (*a*) Fatty acid, long-chain alcohol.
  - (b) Glycerol, fatty acid.
  - (c) Carbohydrate, long-chain alcohol.
- **3.** The number of *cis* double bonds. Each *cis* double bond causes a bend in the hydrocarbon chain; it is more difficult to pack these bent chains in the crystal lattice.
- **4.** The definition of substances such as lipids is based, not on a common structure, but on their solubilities in water and in nonpolar solvents.
- 5. Both compounds should yield sphingosine and a fatty acid upon strong alkaline hydrolysis. Phosphocholine is produced only from sphingomyelin; cerebroside produces one or more sugars, but no phosphate.
- **6.** Strong alkaline hydrolysis of phosphatidylcholine released 2 fatty acids per phosphate in PC; the same treatment of sphingomyelin produces 1 fatty acid per phosphate, as well as sphingosine.
- 7. No, only soluble fibre (in oat bran, fruits and vegetables) does. Insoluble fibre (in wheat bran and beans) does not.
- 8. Not much. About one tablespoon of oil a day will supply all the fat one needs.
- **9.** No. This diet is high in fat and low in complex carbohydrates. Just the opposite of good nutrition.
- **10.** Tea oil, which is cold-pressed from tea seeds, is unrefined and low in saturated fat like olive oil. But tea oil is a better choice for frying because it resists breaking down into *trans* fats when heated. It also has a naturally neutral flavour.

# CHAPTER - 13

1. Hydrophobic units: (a) 2 fatty acids; (b), (c), and (d) 1 fatty acid and the hydrocarbon chain of sphingosine; (e) the hydrocarbon backbone.

*Hydrophilic units*: (*a*) phosphoethanolamine; (*b*) phosphocholine; (*c*) D-galatose; (*d*) several sugar molecules; (*e*) alcohol group(–OH)

2. (e) anthocyanin pigments

# CHAPTER - 14

- 1. Unsaturated fats (e.g., olive oil) are susceptible to oxidation by molecular oxygen.
- 2. (a) The sodium salts of palmitic and stearic acids, plus glycerol
  - (b) The sodium salts of palmitic and oleic acids, plus glycerol-3-phosphorylcholine.
- **3.** The triacylglycerols of animal fats (grease) are hydrolyzed by NaOH, in a process known as saponification, to form soaps, which are much more soluble in water than are the triacylglycerols.
- **4.** Eight different triacylglycerols can be constructed. All saturated (palmitic) fatty acids, all unsaturated (oleic) fatty acids, or any combination of oleic and palmitic acids can be used. Furthermore, positional isomers are possible, as the three carbons of glycerol are not equivalent. In order of increasing melting point: OOO, OOP and OPO; PPO and POP; PPP, where O = oleic, P = palmitic.
- 5. In order of increasing solubility: triacylglycerol; diacylglycerol; monoacylglycerol.
- 6. Eggs contain rich proteins composed of many amino acids. On heating eggs, their proteins coagulate into a solid mass. 'Ghee' is a mixture of more than one fatty acids, which may be saturated or unsaturated. These fatty acids soften at high temperatures and subsequently melt. In the case of eggs, the reaction is irreversible, but it is reversible in the case of 'ghee'.
- 7. Exercise gets rid of fat but increases muscle which weighs more. Muscles are denser and take less space than fat.
- **8.** Obesity is the result of caloric intake in excess of body needs. On a per-gram-of-diet basis, a diet rich in fat is more likely to lead to obesity than a diet rich in sugar because the former contains a higher caloric content per grain.
- **9.** No. The amount of fat that you lose depends on the number of calories you burn, not the intensity of the workout.
- 10. Olive, canola, peanut and sesame seed oils. Olive oil has the most.
- 11. A little better, provided you use the tub or liquid type and use it sparingly.
- 12. Surface tension of water is so strong that it does not allow water to form stable bubbles when blown through a pipe. Soaps and detergents contain a basic cleaning agent called surfactant or surface-active agent. Surfactants lower the surface tension of water sufficiently to enable a film of soap solution to be blown as bubbles. So soapy water is used by children to blow bubbles.
- **13.** As paper is made of cellulose, when we write with a fountain pen, the colouring substance in the ink enters the fine capillaries through capillary action. When the solvent evaporates, dry ink remains in the capillaries, thus making the visible mark on the paper. If the surface of the paper is oily, the oil repels the ink which as a result does not stick to the paper to produce a mark. So it is not possible to write on oily paper with a fountain pen.

In the case of a ballpoint pen, when drawn over the oily surface, the ball on the tip of a ballpoint pen slips and does not rotate as there is no friction. As a result, the thick ink in it does not flow out and does not write.

14. Butter is nothing but solidified milk fat obtained from cream or whole milk by churning. Butter turns rancid if left unrefrigerated for some time because of the formation of butyric

acid by the action of oxygen of air or due to bacterial action. Butyric acid is present in butter in the form of glycerol ester. This ester breaks down into butyric acid and butyl alcohol by the action of oxygen of air or due to bacterial action when kept at room temperature for a long time. It is the butyric acid that imparts the strong unpleasant smell to rancid butter. Refrigeration reduces the bacterial action and good packaging, the action of oxygen.

- **15.** Bubbles are spherical in shape because of the surface tension of liquids. Soap bubbles are formed by blowing air into a film of soap water. *Soap is a surfactant, a chemical which when added to water reduces its surface tension. In other words, it makes the film to stretch more without breaking.* Therefore, the bubble formed from soap solution lasts longer. On the other hand, a water bubble bursts as soon as it is formed because of the higher surface tension of water.
- 16. Vegetable oils are mixtures of chemicals called glycerides or esters of glycerides and long chain fatty acids. Oil is obtained by crushing oil-bearing seeds such as groundnut, sunflower seeds, or rapeseed, and then pressing the oil through expellers. These mechanically-extracted oils contain impurities like gums and free fatty acids (FFAs), which have to be removed to make the oils suitable cooking media. Refining of oil is done by first treating it with alkali, which forms soap with the FFAs. The soaps settle out carrying with them some colouring matter. The colour and odour are removed by treating the oil with some absorbing material like Fuller's earth. Refining can also be done by extracting the pure oil with a suitable organic solvent like hexane and then removing the solvent by distillation.
- 17. Any substance which is soluble in water will completely dissolve in it and form a clear and transparent solution. But oil-based substances are immiscible with water and so they form a fine emulsion. Since dettol and phenyls contain substances that are immiscible with water, they do not mix when added to the water. However, they also contain some chemicals which act as surfactants or detergents that help in breaking up of the oily layer into small droplets. This makes dettol or phenyl to form a fine emulsion when added to water and make it appear cloudy. Since the emulsion is formed of fine droplets of the immiscible liquid and the amount of dettol or phenyl added is also quite small, the emulsion stays and does not separate out into a different oily layer on standing.

- **1.** (*a*) TTGATC; (*b*) GTTCGA; (*c*) ACGCGT; (*d*) ATGGTA.
- **2.** (a) [T] + [C] = 0.46, (b) [T] = 0.30, [C] = 0.24, and [A] + [G] = 0.46.
- **3.** (*a*) 5' -UAACGGUACGAU-3'
  - (b) Leu-Pro-Ser-Asp-Trp-Met
  - (c) Poly(Leu-Leu-Thr-Tyr)
- 4. The 2'-OH group in RNA acts as an intramolecular nucleophil. In the alkaline hydrolysis of RNA, it forms a 2'-3' cyclic intermediate.
- 5. (a) There are long stretches of each because the transition is highly cooperative.
  (b) B-Z junctions are energetically highly unfavourable.
  (c) A-B transitions are less cooperative than B-Z transitions because the helix stays right-handed at an A-B junction but not at a B-Z junction.
- 6. The sequence of the coding (+, sense) strand is 5'-ATGGGGAACAGCAAGAGTGGGGCCCTGTCCAAGGAG-3' and the sequence of template (-, antisense) strand is

## 3' -TACCCCTTGTCGTTCTCACCCCGGGACAGGTTCCTC-5'

- **7.** An error will only affect one molecule of mRNA of many synthesized from a gene. In addition, the errors do not become a permanent part of the genomic information.
- **8.** At any given instant, only a fraction of the genome (total DNA) is being transcribed. Consequently, speed is not necessary.
- 9. (a) It must be a single-strand DNA, since Chargaff's rules are not obeyed.
- (b) It should be mostly random coil, with perhaps some self-bonding into hairpins, etc. **10.** (a)  ${}^{3'}TGGCATTCCGAAATC^{5'}$ .
  - (b) <sup>5'</sup>pApCpCpGpTpApApGpGpCpTpTpTpApGp<sup>3'</sup>.
     (c) <sup>3'</sup>UGGCAUUCCGAAAUC<sup>5'</sup>.
- 11. N-3, N-7, and N-9.
- 12. (3') TACGGGCATACGTAAG (5').
- **13.**  $0.94 \times 10^{-3}$  g
- 14. The RNA helix will be in the A conformation; the DNA helix will generally be in the B conformation.
- **15.** In eukaryotic DNA, about 5% of cytosine residues are methylated. 5-methylcytosine can spontaneously deaminate to form thymine, and the resulting G–T pair is one of the most common mismatches in eukaryotic cells.
- **16.** Base stacking in nucleic acids tends to reduce the absorption of UV light. Denaturation of DNA involves the loss of base stacking, and UV absorption increases.
- 17. One DNA contains 32% A, 32% T, 18% G, and 18% C; the other 17% A, 17% T, 33% G, and 33% C. This assumes that both are double-stranded. The DNA containing 33% G and 33% C almost certainly came from the thermophilic bacterium; its higher  $G \equiv C$  content makes it much more stable to heat.
- 18. The coding strand of the gene has the same sequence as the mRNA (except U replaces T in the RNA). In HbA, the codon at position 142 of mRNA is a stop codon so the last amino acid added is 141. In Hb Constant Spring, a point mutation has mutated the DNA so that the mRNA codon at 142 now codes for an amino acid instead of stop. Translation continues until a stop codon appears at position 173 (so 172 amino acids). This could be a transition mutation—pyrimidine for pyrimidine.
- 19. Thymine is derived almost exclusively from DNA. The degradation of thymine leads to the unique product  $\beta$ -aminoisobutyrate, which is excreted. This can be measured in urine.
- **20.** (*a*) TTGATC
  - (**b**) GTTCGA
  - (c) ACGCGT
  - (d) ATGGTA
- 21. 5'-UAACGGUACGAU-3'

- **1.** (*a*) hydrolase
  - (b) lyase
  - (c) transferase
  - (d) hydrolase
  - (e) reductoisomerase
  - (f) lyase

# Contents

#### **1178** FUNDAMENTALS OF BIOCHEMISTRY

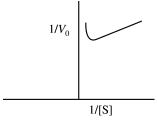
- (g) transferase
- (h) lyase
- (i) isomerase
- (j) hydrolase
- (k) isomerase
- (l) transferase

# CHAPTER - 17

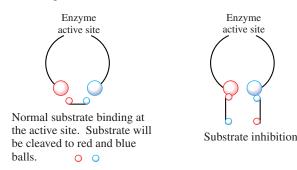
- 1. The activity of the enzyme that converts sugar to starch is destroyed by heat denaturation.
- **2.** Glu<sup>35</sup> : protonated; Asp<sup>52</sup>: deprotonated. The pH-activity profile suggests that maximum catalytic activity occurs when Glu<sup>35</sup> is protonated and Asp<sup>52</sup> is deprotonated.
- **3.** (*d*) they will bind one substrate only.
- 4. Cuts on the tongue heal fast because the tongue is highly vascularized that is, has plenty of blood vessels. The rich supply of blood means that white blood corpuscles can easily reach the site of the wound and carry out defense functions preventing infection by bacteria. The secondary infection can prolong healing. The saliva too helps in this as it bathes the tongue in a chemical called lysozyme that has mildly antiseptic properties. Besides, the epithelial cells of the tongue divide very rapidly and so the wounds in the mouth and on the tongue heal fast.

## **CHAPTER - 18**

- **1.**  $11 \mu \text{mol minute}^{-1}$
- **2.** (*a*)



(b) This behaviour is substrate inhibition—at high concentrations, the substrate forms unproductive complexes at the active site. The drawing below shows what might occur, Substrate normally binds in a defined orientation, shown in the drawing as red to red and blue to blue. At high concentrations, the substrate may bind at the active site such that the proper orientation is met for each end of the molecule, but two different substrate molecules are binding.



**3.** (*a*) 18.8 nm

(b) Three-dimensional folding of the enzyme brings these amino acid residues into close proximity,

(c) The protein serves as "scaffolding" to keep the catalytic groups in a precise orientation. Also, many other interactions occur between the enzyme and its substrate, and some of the binding energy derived from these interactions contributes to catalysis.

- **4.** (a)  $1.7 \times 10^{-3}$  m (b) 0.33; 0.67; 0.91.
- 5.  $K_{\rm m} = 2.2 \text{ mM}; V_{\rm max} = 0.51 \text{ µmol/min.}$ 6. (a)  $k_{\rm cat} = 2.0 \times 10^7 \text{ min}^{-1}$ 
  - (b)  $\Delta G^{\ddagger} = 43.3 \text{ kJ/mol}$  (at 37 °C or 310 K) (c)  $\Delta G^{\ddagger} = 83.2 \text{ kJ/mol}$
- 7. 29,000; it is assumed that each enzyme molecule contains only one titratable sulfhydryl group.
- 8. The enzyme–substrate complex is more stable than the enzyme alone.
- 9. The best way to handle the data is to take the reciprocals of both [S] and v and construct a Lineweaver–Burk plot. You should find that the two curves cross the y-axis at the same point but the curve in the presence of A crosses the x-axis closer to the origin. This pattern indicates that A is a competitive inhibitor.

10.	$-1/K_{\rm m}$	<b>K</b> <sub>m</sub>	$1/V_{\text{max}}$	V <sub>max</sub>
Absence of A	-0.14	7.1	0.8	1.25
Presence of A	-0.08	12.5	0.8	1.25

With a competitive inhibitor  $V_{\text{max}}$  remains constant (be sure you understand why) but the apparent  $K_{\rm m}$  is larger. It takes more substrate to reach a given velocity because the substrate has to compete with the inhibitor

#### **CHAPTER - 19**

1.	Equation	RQ
	(a) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$	0.67*
	(b) $CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O$	1.0
	(c) $CH_3(CH_2)_{16}COOH + 26O_2 \longrightarrow 18CO_2 + 18H_2O$	0.69
	(d) $CH_3(CH_2)_{14}$ (CH) <sub>2</sub> COOH + 25 <sup>1</sup> / <sub>2</sub> O <sub>2</sub> $\longrightarrow$ 18CO <sub>2</sub> + 17H <sub>2</sub> O	0.71
	(e) $CH_3(CH_2)_{12}$ (CH) <sub>4</sub> COOH + 25O <sub>2</sub> $\longrightarrow$ 18CO <sub>2</sub> + 16H <sub>2</sub> O	0.71
	*Example : $RQ = 2CO_2/3O_2$ .	

- 1. Reactions in parts a and c, to the left; reactions in parts b and d, to the right.
- 2. None whatsoever.
- **3.** (a)  $\Delta G^{0'} = +7.5 \text{ kcal mol}^{-1} (+31.4 \text{ kJ mol}^{-1}) \text{ and } K'_{eq} = 3.2 \times 10^{-6} (b) 3.28 \times 10^{4}$ 4. (a) Acetate + CoA +  $H^+$  goes to acetyl-CoA +  $H_2O$ ,
  - $\Delta G^{0'}$  = +7.5 kcal mol<sup>-1</sup> (+31.4 kJ mol<sup>-1</sup>). ATP hydrolysis,
  - $\Delta G^{0'} = -10.9 \text{ kcal mol}^{-1} (-45.6 \text{ kJ mol}^{-1})$ . Overall reaction,
  - $\Delta G^{0'} = -3.4 \text{ kcal mol}^{-1} (-14.2 \text{ kJ mol}^{-1}).$
  - (b) With pyrophosphate hydrolysis,  $\Delta G^{0'} = -8.0 \text{ kcal mol}^{-1} (-33.4 \text{ kJ mol}^{-1})$ .

5. (a) For an acid AH, AH  $\square \square \square$   $A^- + H^+$ ,  $K = \frac{[A^-][H^+]}{[AH]}$ .

The pK is defined as  $pK = -\log_{10} K$ .  $\Delta G^{0'}$  is the standard free energy change at pH 7. Thus,  $\Delta G^{0'} = -RT$  In K = -2.303  $\log_{10} K = -2.303$  (pK -7) kcal mol<sup>-1</sup> since [H<sup>+</sup>] =  $10^{-7}$  M.

(**b**) 
$$\Delta G^0 = -2.303 \ (4.8 \ -7) = -5.1 \ \text{kcal mol}^{-1} \ (-21.3 \ \text{kJ mol}^{-1}).$$

- 6. An ADP unit.
- 7. Recall that  $\Delta G = \Delta G^{0'} + RT$  In [products/reactants]. Altering the ratio of products to reactants will cause  $\Delta G$  to vary. In glycolysis, the concentrations of the components of the pathway result in a value of  $\Delta G$  greater than that of  $\Delta G^{0'}$ .
- **8.** (*a*)  $\Delta G^0 = -2872$  kJ/mol
  - (**b**)  $\Delta G^0 = -1694 \text{ kJ/mol}$
  - (**c**) 41%
- **9.** (a)  $K = 5.44 \times 10^{-2}$ ;  $(f_{G3P})_{eq} = 0.052$ 
  - (**b**)  $\Delta G = -4.37$  kJ/mol
- 10. (a)  $\Delta S$  must be positive, because the increase in available states corresponds to an increase in entropy.

(b) Since  $\Delta G = \Delta H - T\Delta S$ , a positive  $\Delta S$  yields a negative contribution to  $\Delta G$  (*T* is always a positive number). Thus, for proteins to be stable, which requires  $\Delta G$  for the above to be positive, denaturation must involve a large positive  $\Delta H$  and/or an additional negative contribution to  $\Delta S$ . In fact, both occur.

- 11. No, because the repulsion between  $ADP^{2^-}$  and  $P_i^{2^-}$  is less than that between  $ADP^{3^-}$  and  $ADP^{2^-}$ , and the release of an H<sup>+</sup> will change the value as well.
- 12.  $\Delta G^{0'} = -RT \ln K'_{eq} = -2.303 RT \log K'_{eq}$ . Substitution gives  $\log K'_{eq} = 5. K'_{eq}$  then is 1,00,000 so the B/A = 1,00,000/1.
- 13. Acetylcholine is an excitatory neurotransmitter, causing channels to open, Na<sup>+</sup> to enter, and a depolarization of the membrane. Hydrolysis of acetylcholine allows repolarization. The presence of the inhibitor keeps the channel open and prevents repolarization, and thus continued transmission of nerve impulses.
- 14. (a) 4.75 J/mol (b) -7.6 J/mol (c) 13.7 kJ/mol
- **15.** (*a*) 261 м (*b*) 609 м (*c*) 0.29
- **16.** (*a*) -1.7 kJ/mol (*b*) 4.4 kJ/mol

(c) At a given temperature, the value of  $\Delta G^{0'}$  for any reaction is fixed and is defined for standare conditions (both fructose-6-phosphate and glucose-6-phosphate at 1<sub>M</sub>). In contrast,  $\Delta G$  is a variable that can be calculated for any set of reactant and product concentrations.

17. Less. The overall equation for ATP hydrolysis can be approximated as :

 $ATP^{4-} + H_2O \longrightarrow ADP^{3-} + HPO_4^{2-} + H^+$ 

(This is only an approximation because the ionized species shown here are the major, but not the only, forms present). Under standard conditions (*i.e.*,  $[ATP] = [ADP] = [P_i] = 1$  M), the concentration of water is 55 m and does not change during the reaction. Because H<sup>+</sup> ions are produced in the reaction, at a higher [H<sup>+</sup>] (pH 5.0) the equilibrium would be shifted to the left and less free energy would be released.

- **18.** 9.6
- 19. 10.0 kJ/mol

- **20.** (*a*) 1.1 s
  - (b) Phosphocreatine + ADP  $\rightarrow$  creatine + ATP.
  - (c) ATP synthesis coupled to the catabolism of glucose, amino acids, and fatty acids.
- **21.** (*a*) 0.8 kJ/mol

(b) Inorganic pyrophosphatase catalyzes the hydrolysis of pyrophosphate and drives the net reaction toward the synthesis of acetyl-CoA.

- **22.** (a) 1.14 V (b) –220 kJ/mol (c) About 7
- **23.** In order of increasing tendency : (a); (d); (b); (c)
- 24. An anabolic reaction consumes ATP; a catabolic reaction generates ATP.
- 25. In ATP and other compounds containing high-energy phosphates, and in glycogen.
- **26.** (a) nucleotides
- **27.** (*d*) an energy-donor substance or a coenzyme
- 28. (c) chloroplasts and mitochondria both

## CHAPTER - 21

- 1. Hexokinase has a low ATPase activity in the absence of a sugar because it is in a catalytically inactive conformation. The addition of xylose closes the cleft between the two lobes of the enzyme. However, xylose lacks a hydroxymethyl group, and so it cannot be phosphorylated. Instead, a water molecule at the site normally occupied by the C-6 hydroxymethyl group acts as the acceptor of the phosphoryl group from ATP.
- 2. (a) The fructose-1-phosphate pathway forms glyceraldehyde 3-phosphate.

(b) Phosphofructokinase, a key control enzyme, is bypassed. Furthermore, fructose 1-phosphate stimulates pyruvate kinase.

- **3.** Fructose 2,6-bisphosphate, present at high concentration when glucose is abundant, normally inhibits gluconeogenesis by blocking fructose 1,6-bisphosphatase. In this genetic disorder, the phosphatase is active irrespective of the glucose level. Hence, substrate cycling is increased. The level of fructose 1,6-bisphosphate is consequently lower than normal. Less pyruvate is formed and thus less ATP is generated.
- **4.** There will be no labeled carbons. The CO<sub>2</sub> added to pyruvate (formed from the lactate) to form oxaloacetate is lost with the conversion of oxaloacetate into phosphoenolpyruvate.
- 5. This example illustrates the difference between *stoichiometric* and *catalytic* utilization of a molecule. If cells used NAD<sup>+</sup> stoichiometrically, a new molecule of NAD<sup>+</sup> would be required each time a lactate is produced. As we will see, the synthesis of NAD<sup>+</sup> requires ATP. On the other hand, if the NAD<sup>+</sup> that is converted into NADH could be recycled and reused, a small amount of the molecule could regenerate a vast amount of lactate. This is the case in the cell. NAD<sup>+</sup> is regenerated by the oxidation of NADH and reused. NAD<sup>+</sup> is thus used catalytically.
- 6. Galactose is a component of glycoproteins. Possibly, the absence of galactose leads to the improper formation or function of glycoproteins required in the central nervous system. More generally, the fact that the symptoms arise in the absence of galactose suggests that galactose is required in some fashion.

7. Glc 
$$\longrightarrow$$
 G6P  $\longrightarrow$  G1P  $\longrightarrow$  UDP-Glc  $\longrightarrow$  UDP-Gal  $\xrightarrow{}_{Glc}$  lactose  
2 Glucose + ATP + UTP  $\longrightarrow$  lactose + ADP + UDP + PPi

**8.** (*a*) 2 (glycolysis).

- (b) 6 (gluconeogenesis requires ATP).
- 9. Net equation : Glucose + 2ATP  $\rightarrow$  2 glyceraldehyde-3-phosphate + 2ADP + 2H<sup>+</sup>  $\Delta G^{0}$  = 2.34 kJ/mol
- **10.** Net equation :

Glyceraldehyde-3-phosphate + 2ADP + Pi +  $H^+ \rightarrow lactate + 2ATP + H_2O$  $\Delta G^{0'} = -63 \text{ kJ/mol}$ 

- **11.** The glucose in cells is phosphorylated to glucose-6-phosphate. Because the equilibrium of this reaction strongly favours the product, glucose that enters the cell is rapidly and irreversibly converted to glucose-6-phosphate.
- 12. Net equation : Glycerol + 2NAD<sup>+</sup> + ADP + P<sub>i</sub>  $\rightarrow$  pyruvate + 2NADH + ATP + 2H<sup>+</sup>
- 13. (a) Increases (b) Decreases (c) Increases.
- 14. *Resting* : [ATP] high; [AMP] low; [acetyl-CoA] and [citrate] intermediate. *Running* : [ATP] intermediate; [AMP] high; [acetyl-CoA] and [citrate] low. Glucose flux through glycolysis increases during the anaerobic sprint, because: (1) the ATP inhibition of glycogen phosphorylase and PFK-1 is partially relieved, (2) AMP stimulates both enzymes, and (3) lower [citrate] and [acetyl-CoA] relieves their inhibitory effects on PFK-1 and pyruvate kinase, respectively.
- **15.** The migrating bird relies on the highly efficient aerobic oxidation of fats, rather than the anaerobic metabolism of glucose used by a sprinting rabbit. The bird reserves its muscle glycogen for short bursts of energy during emergencies.
- 16. Anaerobically, there is a net of 2 mol ATP/mol glucose. Aerobically, the same net of 2 ATP is obtained plus 2 NADH because pyruvate is the product. Let us assume the cell uses the malate-aspartate shuttle where each NADH yeilds 2½ ATP. Thus, there is a net of 7 mol ATP/mol glucose. Each pyruvate is converted to AcCoA and the AcCoA is oxidized by the tricarboxylic acid cycle. Each mole of pyruvate then yields 12.5 mol ATP or 25 mol ATP for the 2 pyruvates. This gives a total of 32 mol ATP/mol glucose aerobically. Therefore, glycolysis must proceed 16 times as rapidly under anaerobic conditions to generate the same amount of ATP as occurs aerobically.

## **CHAPTER - 22**

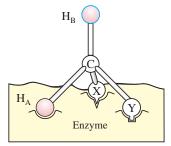
- **1.**  $-9.8 \text{ kcal mol}^{-1}$  (-41.0 kJ mol}{-1}).
- 2. Enzymes or enzyme complexes are biological catalysts. Recall that a catalyst facilitates a chemical reaction without the catalyst itself being permanently altered. Oxaloacetate can be thought of as a catalyst because it binds to an acetyl group, leads to the oxidative decarboxylation of the two carbon atoms, and is regenerated at the completion of a cycle. In essence, oxaloacetate (and any cycle intermediate) acts as a catalyst.
- 3. A decrease in the amount of  $O_2$  will necessitate an increase in anaerobic glycolysis for energy production, leading to the generation of a large amount of lactic acid. Under conditions of shock, the kinase inhibitor is administered to ensure that pyruvate dehydrogenase is operating maximally.
- **4.** (*a*) The steady-state concentrations of the products are low compared with those of the substrates.

(b) The ratio of malate to oxaloacetate must be greater than  $1.75 \times 10^4$  for oxaloacetate to be formed.

**5.** The enol intermediate of acetyl-CoA attacks the carbonyl carbon atom of glyoxylate to form a C–C bond. This reaction is like the condensation of oxaloacetate with the enol

intermediate of acetyl-CoA in the reaction catalyzed by citrate synthase. Glyoxylate contains a hydrogen atom in place of the  $- CH_2COO^-$  group of oxaloacetate; the reactions are otherwise nearly identical.

6. Call one hydrogen atom A and the other B. Now suppose that an enzyme binds three groups of this substrate—X, Y, and H—at three complementary sites. The adjoining diagram shows X, Y, and H<sub>A</sub> bound to three points on the enzyme. In contrast X, Y, and H<sub>B</sub> cannot be bound to this active site; two of these three groups can be bound, but not all three. Thus, H<sub>A</sub> and H<sub>B</sub> will have different fates.



Sterically nonequivalent groups such as  $H_A$  and  $H_B$  will almost always be distinguished in enzymatic reactions. The essence of the differentiation of these groups is that the enzyme holds the substrate in a specific orientation. Attachment at three points, as depicted in the diagram, is a readily visualized way of achieving a particular orientation of the substrate, but it is not the only means of doing so.

- 7. C-1: all released as CO<sub>2</sub>. C-2 and C-3: all retained in oxaloacetate.
- **8.** C-3 and C-4, since these become the carboxyl group of pyruvate, which is lost in the pyruvate dehydrogenase reaction.
- **9.** Because NADH and acetyl-CoA activate the enzyme, it makes metabolic sense to expect that NAD<sup>+</sup> and CoA-SH would be inhibitory, and these inhibitions are observed.
- **10.** Some possible mechanisms: substrate-level control of citrate synthase, activation of citrate lyase by acetyl-CoA or fatty acids, inhibition of isocitrate lyase by succinate (to ensure adequate flux through the citric acid cycle).
- **11.** 2 Acetyl-CoA + 2NAD<sup>+</sup> + FAD +  $3H_2O \rightarrow$

oxaloacetate + 2NADH +  $FADH_2$  + 2CoA-SH +  $4H^+$ 

- 12.  $\text{NAD}^+$  +  $\text{FADH}_2 \implies \text{NADH} + \text{FAD} + \text{H}^+$  $\text{NAD}^+$  can oxidize  $\text{FADH}_2$  if its local concentration is much higher than that of  $\text{FADH}_2$ .
- **13.**  $[NAD^+]/[NADH]$  should be high, so that it can promote the oxidation of substrates, *e.g.*, malate + NAD<sup>+</sup>  $\implies$  oxaloacetate + NADH + H<sup>+</sup>. Conversely, since NADPH and NADP<sup>+</sup> usually promote reduction of substrates, we expect [NADP<sup>+</sup>]/[NADPH] to be low.
- 14. No. For every two carbons that enter as acetate, two leave the cycle as  $CO_2$ ; thus there is no net synthesis of oxaloacetate. Net synthesis of oxaloacetate occurs by the carboxylation of pyruvate, an anaplerotic reaction.
- **15.** Net reaction :

2 Pyruvate + ATP + 2NAD<sup>+</sup> + H<sub>2</sub>O  $\rightarrow$ 

 $\alpha$ -ketoglutarate + CO<sub>2</sub> + ADP + P<sub>i</sub> + 2NADH + 3H<sup>+</sup>

16. Oxygen is needed to recycle NAD<sup>+</sup> from the NADH produced by the oxidative reactions of the citric acid cycle. Reoxidation of NADH occurs during mitochondrial oxidative phosphorylation.

- 17. Steps (4) and (5) are essential in the reoxidation of the reduced lipoamide cofactor.
- 18. The labeled keto carbon of pyruvate becomes the labeled carboxyl carbon of acetyl-CoA. After condensation with oxaloacetate, the first carboxyl group of citrate is labeled. This label is retained through subsequent reactions to succinate. However, succinate is a symmetrical compound to the enzyme so, in effect, both carboxyl groups of succinate are labeled. This means that the oxaloacetate regenerated is labeled in both carboxyl groups at the end of one turn (actually half the molecules are labeled in one carboxyl and half in the other but this can't be distinguished experimentally). Note that CO<sub>2</sub> is not labeled. In the second turn, the same carboxyl labeled acetyl-CoA is added but this time to labeled oxaloacetate. Both carboxyl groups of the oxaloacetate are released as CO<sub>2</sub> so it will be labeled, as will the regenerated oxaloacetate.
- **19.** In the absence of oxygen, the citric acid cycle is inactive, and less ATP is generated per molecule of glucose.
- **20.** (*d*) matrix
- **21.** (a) a bacterium

## CHAPTER - 23

- **1.** (a) 12.5; (b) 14; (c) 32; (d) 13.5; (e) 30; (f) 16.
- 2. Biochemists use  $E_0'$ , the value at pH 7, whereas chemists use  $E_0$ , the value in 1 M H<sup>+</sup>. The prime denotes that pH 7 is the standard state.
- **3.** (*a*) Blocks electron transport and proton pumping at Complex III.

(b) Blocks electron transport and ATP synthesis by inhibiting the exchange of ATP and ADP across the inner mitochondrial membrane.

(c) Blocks electron transport and proton pumping at Complex I.

(*d*) Blocks ATP synthesis without inhibiting electron transport by dissipating the proton gradient.

(e) Blocks electron transport and proton pumping at Complex III.

- (f) Blocks electron transport and proton pumping at Complex II.
- **4.** (*a*) The P: O ratio is equal to the product of  $(H^+/2e^-)$  and  $(\sim P/H^+)$ . Note that the P:O ratio is identical with the (P:  $2e^-$ ) ratio,

(**b**) 2.5 and 1.5, respectively.

- 5. Cyanide can be lethal because it binds to the ferric form of cytochrome oxidase and thereby inhibits oxidative phosphorylation. Nitrite converts ferrohemoglobin into ferrihemoglobin, which also binds cyanide. Thus, ferrihemoglobin competes with cytochrome oxidase for cyanide. This competition is therapeutically effective because the amount of ferrihemoglobin that can be formed without impairing oxygen transport is much greater than the amount of cytochrome oxidase.
- **6.** Such a defect (called **Luft syndrome**) was found in a 38-year-old woman who was incapable of performing prolonged physical work. Her basal metabolic rate was more than twice normal, but her thyroid function was normal. A muscle biopsy showed that her mitochondria were highly variable and atypical in structure. Biochemical studies then revealed that oxidation and phosphorylation were not tightly coupled in these mitochondria. In this patient, much of the energy of fuel molecules was converted into heat rather than ATP.
- **7.** If oxidative phosphorylation were uncoupled, no ATP could be produced. In a futile attempt to generate ATP, much fuel would be consumed. The danger lies in the dose. Too

much uncoupling would lead to tissue damage in highly aerobic organs such as the brain and heart, which would have severe consequences for the organism as a whole. The energy that is normally transformed into ATP would be released as heat. To maintain body temperature, sweating might increase, although the very process of sweating itself depends on ATP.

- 8. Add the inhibitor with and without an uncoupler, and monitor the rate of  $O_2$  consumption. If the  $O_2$  consumption increases again in the presence of inhibitor and uncoupler, the inhibitor must be inhibiting ATP synthase. If the uncoupler has no effect on the inhibition, the inhibitor is inhibiting the electron-transport chain.
- **9.** Because the energy not used for ATP was dissipated as heat, and the subjects developed uncontrollable fevers.
- 10. Reaction (1): (a), (d) NADH; (b) E-FMN; (c) NAD<sup>+</sup>/ NADH and E-FMN/FMNH<sub>2</sub> Reaction (2): (a), (d) E-FMNH<sub>2</sub>; (b), (e) Fe<sup>3+</sup>; (c) E-FMN/FMNH<sub>2</sub> and Fe<sup>3+</sup>/Fe<sup>2+</sup> Reaction (3): (a), (d) Fe<sup>2+</sup>; (b), (e) UQ; (c) Fe<sup>3+</sup>/Fe<sup>2+</sup> and UQ/UQH<sub>2</sub>.
- 11. (a) NAD<sup>+</sup>/NADH (b) Pyruvate/lactate (c) Lactate formation (d) -25 kJ/mol (e)  $2.58 \times 10^4$
- **12.** (a) External medium:  $4.0 \times 10^{-8}$  M; Matrix  $2.0 \times 10^{-8}$  M (b) 2 : 1 (c) 21 (d) No (e) From the transmembrane potential.
- **13.** About 70  $\mu$  mol/s g. With a steady state [ATP] of 7  $\mu$ mol/g, this is equivalent to 10 turnovers of the ATP pool per second; the reservoir would last about 0.1 s.
- **14.** (c) cytochromes

- The absence of ketone bodies is due to the fact that the liver, the source of blood-ketone bodies, cannot oxidize fatty acids to produce acetyl-CoA. Moreover, because of the impaired fatty acid oxidation, the liver becomes more dependent on glucose as an energy source. This dependency results in a decrease in gluconeogenesis and a drop in bloodglucose levels, which is exacerbated by the lack of fatty acid oxidation in muscle and a subsequent increase in glucose uptake from the blood.
- Peroxisomes enchance the degradation of fatty acids. Consequently, increasing the activity
  of peroxisomes could help to lower levels of blood triacylglycerides. In fact, clofibrate
  is rarely used because of serious side effects.
- **3.** (*a*) Fats burn in the flame of carbohydrates. Without carbohydrates, there would be no anaplerotic reactions to replenish the TCA-cycle components. With a diet of fats only, the acetyl-CoA from fatty acid degradation would build up.
  - (b) Acetone from ketone bodies.
  - (c) Yes. Odd-chain fatty acids would lead to the production of propionyl CoA, which can be converted into succinyl CoA, a TCA-cycle component. It would serve to replenish the TCA cycle and mitigate the halitosis.
- **4.** A labeled fat can enter the citric acid cycle as acetyl-CoA and yield labeled oxaloacetate, but only after two carbon atoms have been lost as  $CO_2$ . Consequently, even though oxaloacetate may be labeled, there can be no net synthesis in the amount of oxaloacetate and hence no net synthesis of glucose or glycogen.
- **5.** Adipose tissue lacks glycerol kinase. Glycolysis generates dihydroxyacetone phosphate, which is reduced to glycerol 3-phosphate.

6. (a) Malonyl-CoA at high levels inhibits carnitine acyltransferase I, and this inhibits ketogenesis by blocking the transport of fatty acids into mitochondria, both for  $\beta$ -oxidation and for ketogenesis.

(b) The high  $K_{\rm M}$  of glucokinase, a liver-specific enzyme, allows the liver to control the rate of glucose phosphorylation over a wide range of glucose concentrations. Accumulation of glucose-6-phosphate activates the D form of glycogen synthase and promotes glycogen deposition. By several mechanisms, the liver also senses when blood glucose levels are low and mobilizes its glycogen reserves accordingly.

- **7.** Phosphorylation of pyruvate kinase by cyclic AMP-dependent protein kinase. The phosphorylated form of the enzyme is far less active than the dephosphorylated form.
- 8. Oleic acid has 18 carbons and 1 double bond. Nine Acetyl CoA  $\times$  10 = 90 ATP. Seven reduced flavoproteins  $\times$  1.5 = 10.5 ATP. (*Note* : In one step the flavoprotein reduction is not necessary because the double bond is not present. The isomerase to convert the *cis*-3-enoyl bond to the *trans*-2-enoyl bond does not involve ATP.) Eight NADH  $\times$  2.5 = 20 ATP. Total = 120.5 ATP 2 ~ P (for activation) = 118.5 ~ P/oleic acid.
- 9. β-oxidation proceeds normally but the final thiolase cleavage yields acetyl CoA and propionyl CoA. Propionyl CoA is *not* a substrate for SCAD (short-chain acyl-CoA dehydrogenase) so β-oxidation terminates.
- 10. The fatty acid portion; the carbons in fatty acids are more reduced than those in glycerol.
- **11.** (a)  $4.0 \times 10^5$  kJ (9.5 × 10<sup>4</sup> kcal)
  - (b) 48 days (c) 0.5 lb/day
- **12.** The first step in fatty acid oxidation is analogous to the conversion of succinate to fumarate; the second step, to the conversion of fumarate to malate; the third step, to the conversion of malate to oxaloacetate.
- **13.** Fatty acyl groups condensed with CoA in the cytosol are first transferred to carnitine, releasing CoA, then transported into the mitochondrion, where they are again condensed with CoA. The cytosolic and mitochondrial pools of CoA are thus kept separate, and no radioactive CoA from the cytosolic pool enters the mitochondrion.
- 14. Oxidation of fats releases metabolic water; 0.49 L of water per pound of tripalmitin.
- **15.** Because the mitochondrial pool of CoA is small, CoA must be recycled from acetyl-CoA *via* the formation of ketone bodies. This allows the operation of the  $\beta$ -oxidation pathway, necessary for energy production.
- **16.** (*a*) Glucose yields pyruvate *via* glycolysis, and pyruvate is the main source of oxaloacetate. Without glucose in the diet, [oxaloacetate] drops and the citric acid cycle slows.
  - (b) Odd-numbered; propionate conversion to succinyl-CoA provides intermediates for the citric acid cycle.
    - ОН |

**17.** 
$$CH_3$$
— $CH_2COO^- + 4\frac{1}{2}O_2 + 25ADP + 25P_i + 25H^+ \rightarrow 4CO_2 + 29H_2O + 25AT$ 

**18.** (1) The reduction of  $O_2$  in the respiratory chain :

$$CH_3(CH_2)_{14}COO + 23O_2 \rightarrow 16CO_2 + 16H_2O$$
  
(2) The formation of the anhydride bond in ATP :

 $129Pi + 129ADP + 129AH^+ \rightarrow 129ATP + 129H_2O$ 

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- **1.**(*a*) Oxidation in mitochondria; synthesis in the cytosol.
  - (b) Acetyl-CoA in oxidation ; acyl carrier protein for synthesis.
  - (c) FAD and  $NAD^+$  in oxidation; NADPH for synthesis.
  - (d) L isomer of 3-hydroxyacyl CoA in oxidation; D isomer in synthesis.
  - (e) From carboxyl to methyl in oxidation; from methyl to carboxyl in synthesis.
  - (f) The enzymes of fatty acid synthesis, but not those of oxidation, are organized in a multienzyme complex.
- 2. (a) palmitoleate
  - (**b**) linoleate
  - (*c*) linoleate
  - (*d*) oleate
  - (e) oleate
  - (f) linolenate
- **3.** Decarboxylation drives the condensation of malonyl ACP and acetyl ACP. In contrast, the condensation of two molecules of acetyl ACP is energetically unfavourable. In gluconeogenesis, decarboxylation drives the formation of phosphoenolpyruvate from oxaloacetate.
- **4.** The mutant enzyme would be persistently active because it could not be inhibited by phosphorylation. Fatty acid synthesis would be abnormally active. Such a mutation might lead to obesity.
- **5.** The probability of synthesizing an error-free polypeptide chain decreases as the length of the chain increases. A single mistake can make the entire polypeptide ineffective. In contrast, a defective subunit can be spurned in forming a noncovalent multienzyme complex; the good subunits are not wasted.
- 6. Glycerol + 4ATP + 3 fatty acids + 4  $H_2O \rightarrow$

triacylglycerol + ADP + 3 AMP + 7Pi +  $4H^+$ 

7. Glycerol + 3 ATP + 2 fatty acids +  $2H_2O$  + CTP + serine  $\rightarrow$ 

phosphatidyl serine + CMP + ADP + 2 AMP + 6 Pi +  $3H^+$ 

- 8. (a) CDP-diacylglycerol
  - (b) CDP-ethanolamine
  - (c) acyl CoA
  - (d) CDP-choline
  - (e) UDP-glucose or UDP-galactose
  - (f) UDP-galactose
  - (g) geranyl pyrophosphate
- 9. Probably  $K_{ea}$  is close to unity, because the bond broken is identical to the bond created.
- 10. Acetoacetate + succinyl-CoA → acetoacetyl-CoA + succinate
   Acetoacetyl-CoA + acetyl-CoA → HMG-CoA + CoA-SH
   HMG-CoA + 2NADPH + 2H<sup>+</sup> → mevalonate + 2NADP<sup>+</sup> + CoA-SH
- **11.** By shutting down the pathway leading to aldosterone, this deficiency increases the supply of progesterone available for conversion to sex steroids.
- **12.** Both glucose and fructose are degraded to pyruvate in glycolysis. The pyruvate is converted

to acetyl-CoA by the pyruvate dehydrogenase complex. Some of this acetyl-CoA enters the citric acid cycle, which produces reducing equivalents (NADH and NADPH). Mitochondrial electron transfer to  $O_2$  yields ATP.

**13.** 8 Acetyl-CoA + 15 ATP + 14 NADPH + 9  $H_2O \rightarrow$ 

palmitate + 8 CoA + 15 ADP + 15  $P_i$  + 14 NADP<sup>+</sup> + 2 H<sup>+</sup>

- 14. By using the three-carbon unit malonyl-CoA, the activated form of acetyl-CoA (recall that malonyl-CoA synthesis requires ATP), metabolism is driven in the direction of fatty acid synthesis by the exergonic release of  $CO_2$ .
- 15. The double bond in palmitoleate is introduced by an oxidation catalyzed by fatty acyl-CoA desaturase, a mixed-function oxidase that requires  $O_2$  as a cosubstrate.
- **16.** 3 Palmitate + glycerol + 7 ATP + 4  $H_2O \rightarrow$  tripalmitin + 7 ADP + 7 $P_i$  + 7 $H^+$
- **17.** Net reaction :

Dihydroxyacetone phosphate + NADH + palmitate +

oleate + 3 ATP + CTP + choline + 4  $H_2O \rightarrow$ 

phosphatidylcholine + NAD<sup>+</sup> + 2 AMP + ADP + H<sup>+</sup> + CMP + 5 P*i*; 7 ATP per molecule of PC.

- 18. The pathways to mevalonate and ketone bodies have steps in common. A decrease in HMG-CoA reductase results in the accumulation of HMG-CoA. This is a substrate for HMG-CoA lyase, which produces acetoacetate. Thus, a decreased HMG-CoA reductase activity leads to increased production of acetoacetate.
- 19. FH cells have LDL receptors with normal binding properties as indicated by the bound radioactivity being the same as that of normal cells. They are unable to internalize the receptor-LDL complex so cholesterol synthesis is not inhibited as it is with normal cells. The mutation is most likely on the carboxy terminus of the protein, which is involved in internalization. Make sure you understand why mutation in other regions would not lead to the observed results.
- 20. By binding bile salts, forcing increased excretion, liver has to convert more cholesterol to bile salts. If liver synthesis of cholesterol is inhibited, liver synthesizes more LDL receptors, removing increased LDL particles (and thus cholesterol) from blood. Patients with FH either have no receptors or have non-functioning LDL receptors so liver cannot increase uptake of LDL from blood. Synthesis is reduced but this does not have as dramatic an effect on blood cholesterol.

- **1.** (*a*) Pyruvate
  - (**b**) oxaloacetate
  - (c)  $\alpha$ -ketoglutarate
  - (*d*)  $\alpha$ -ketoisocaproate
  - (e) phenylpyruvate
  - (f) hydroxyphenylpyruvate.
- 2. Ornithine transcarbamoylase (analogous to N-(phosphonacetyl)-L-aspartate, PALA)
- **3.** Benzoate, phenylacetate, and arginine would be given to supply a protein-restricted diet. Nitrogen would emerge in hippurate, phenylacetylglutamine, and citrulline.
- 4. Aspartame, a dipeptide ester (L-aspartyl-L-phenylalanine methyl ester), is hydrolyzed to L-aspartate and L-phenylalanine. High levels of phenylalanine are harmful in

phenylketonurics.

5. (a) Depletion of glycogen stores. When they are gone, proteins must be degraded to meet the glucose needs of the brain. The resulting amino acids are deaminated, and the nitrogen atoms are excreted as urea.

(b) The brain has adapted to the use of ketone bodies, which are derived from fatty acid catabolism. In other words, the brain is being powered by fatty acid breakdown.

(c) When the glycogen and lipid stores are gone, the only available energy source is protein.

**6.** Deamination to α-keto-β-methylvalerate; oxidative decarboxylation to α-methylbutyryl CoA; oxidation to tiglyl CoA; hydration,oxidation and thiolysis yields acetyl-CoA and propionyl CoA; propionyl CoA to succinyl CoA.

7. 
$$-OO^{5}C_{-4}CH_{-2}CH_{-1}COO^{-1}$$
  
 $| | + COO^{-1}COO^{-1}$   
 $CH_{3} NH_{3}$ 

- 8. PLP forms a covalent Schiff base between the aldehyde carbon of the coenzyme and an  $\varepsilon$ -amino group of a lysine residue. Obviously, this bond must be broken for the coenzyme to form a Schiff base with an amino acid substrate.
- **9.** The most straightforward answer is to place the two enzymes in different cell compartments– the catabolic enzyme in mitochondria and the assimilative enzyme in cytosol.

10. (a) 
$$-OOC-CH_2-C-COO^-$$
 Oxaloacetate  
(b)  $-OOC-CH_2-CH_2-C-COO^-$  Oxaloacetate  
(c)  $CH_3-C-COO^-$  Qyruvate  
(d)  $-CH_2-CH_2-C-COO^-$  Phenylpyruvate

- **11.** No; the nitrogen in Ala can be transferred to oxaloacetate *via* transamination, to form Asp.
- **12.** (*a*) Phenylalanine-4-monooxygenase; a low-phenylalanine diet

(b) The normal route of Phe metabolism *via* hydroxylation to Tyr is blocked, and Phe accumulates

(c) Phe is transformed to phenylpyruvate by transamination, and then to phenyllactate by reduction. The transamination reaction has an equilibrium constant of 1.0, and phenylpyruvate is formed in significant amounts when phenylalanine accumulates.

(d) Because of the deficiency in production of Tyr, a precursor of melanin, the pigment normally present in hair.

- **13.** 17-18 moles of ATP per mole of lactate, depending on which shuttle moves the electrons from NADH produced by the dehydrogenases into the mitochondrion. 15-16 ATP per alanine when nitrogen removal *via* the urea cycle is included.
- 14. The second amino group introduced into urea is transferred from Asp, which is generated during the transamination of Glu to oxaloacetate, a reaction catalyzed by aspartate

aminotransferase. Approximately one half of all the amino groups excreted as urea must pass through the aspartate aminotransferase reaction, making this the most highly active aminotransferase.

**15.** (*a*) A person on a diet consisting only of protein must use amino acids as the principal source of metabolic fuel. Because the catabolism of amino acids requires the removal of nitrogen as urea, the process consumes abnormally large quantities of water to dilute and excrete the urea in the urine. Furthermore, electrolytes in the "liquid protein" must be diluted with water and excreted. If the daily water loss through the kidney is not balanced by a sufficient water intake, a net loss of body water results.

(b) When considering the nutritional benefits of protein, one must keep in mind the total amount of amino acids needed for protein synthesis and the distribution of amino acids in the dietary protein. *Gelatin contains a nutritionally unbalanced distribution of amino acids*. As large amounts of gelatin are ingested and the excess amino acids are catabolized, the capacity of the urea cycle may be exceeded, leading to ammonia toxicity. This is further complicated by the dehydration that may result from excretion of large quantities of urea. A combination of these two factors could produce coma and death.

- **16.** Ala and Gln play special roles in the transport of amino groups from muscle and from other nonhepatic tissues, respectively, to the liver.
- **17.** Tetrahydrobiopterin is a necessary component of phenylalanine, tyrosine, and tryptophan hydroxylases. Its deficiency would inhibit normal degradation of both phenylalanine and tyrosine because their degradative pathways begin with the respective hydroxylases. Catecholamine formation (norepinephrine and epinephrine) begin with the formation of DOPA from tyrosine *via* tyrosine hydroxylase so catecholamine synthesis would be inhibited. The initial step in the conversion of tryptophan to serotonin is catalyzed by tryptophan hydroxylase.
- **18.** Mental retardation seems to be caused by the elevated levels of phenylalanine in the blood so removing phenylalanine from the diet is beneficial. Light skin and hair is a secondary effect of phenylalanine competing with tyrosine for tyrosinase, not an enzyme defect, which is necessary to form melanins. Low tyrosine because of the inability to convert phenylalanine to tyrosine could also be a factor. Since tyrosine is low, the production of catecholamines is affected. If the defect is in the production of tetrahydrobiopterin, diet is less effective because tyrosine hydroxylase leading to DOPA (the first step in catecholamine formation) is tetrahydrobiopterin-dependent.

- 1. Glucose + 2 ADP +  $2P_i$  + 2NAD<sup>+</sup> + 2 glutamate  $\rightarrow$  2 alanine + 2  $\alpha$ -ketoglutarate + 2ATP + 2 NADH +  $2H_2O$  +  $2H^+$
- **2.** The administration of glycine leads to the formation of isovalerylglycine. This watersoluble conjugate, in contrast with isovaleric acid, is excreted very rapidly by the kidneys.
- **3.** The cytosol is a reducing environment, whereas the extracellular milieu is an oxidizing environment.
- 4. Succinyl CoA is formed in the mitochondrial matrix.
- 5. Alanine from pyruvate; aspartate from oxaloacetate; glutamate from  $\alpha$ -ketoglutarate.
- 6. Y could inhibit the C → D step, Z could inhibit the C → F step, and C could inhibit A → B. This scheme is an example of sequential feedback inhibition. Alternatively, Y could inhibit the C → D step, Z could inhibit the C → F step, and the A → B step would be inhibited only in the presence of both Y and Z. This scheme is called concerted

feedback inhibition.

- 7. The rate of the A  $\rightarrow$  B step in the presence of high levels of Y and Z would be 24 s<sup>-1</sup> (0.6 × 0.4 × 100 s<sup>-1</sup>).
- Synthesis from oxaloacetate and α-ketoglutarate would deplete the citric acid cycle, which would decrease ATP production. Anaplerotic reactions would be required to replenish the citric acid cycle.
- **9.** *N*-acetylglutamate is an intermediate in ornithine biosynthesis. Activity of the urea cycle requires both ornithine and carbamoyl phosphate. If insufficient carbamoyl phosphate is available, ornithine will accumulate, and this could cause accumulation of the precursor, *N*-acetylglutamate. This accumulation acts as a signal to stimulate carbamoyl phosphate synthesis to increase urea cycle flux.
- **10.** Because the same enzymes are involved in comparable steps of both isoleucine and valine biosynthesis. Threonine dehydratase.
- **11.** Threonine  $\rightarrow \alpha$ -ketobutyrate: inhibited by isoleucine

 $\alpha$ -ketoisovalerate + acetyl-CoA  $\rightarrow \beta$ -isopropyl malate: inhibited by leucine

Control of valine synthesis is more complicated, because three of the enzymes are involved in synthesis of all three amino acids. One could look for cumulative feedback inhibition– by valine, isoleucine, and leucine – of the first committed reaction :

Pyruvate + hydroxyethyl-TPP  $\longrightarrow \alpha$ -acetolactate

**12.** (a) 5 (c) 5 (b) 3.4 (d) 5

- **13.** Because a pteridine reductase deficiency would impair all tetrahydroiopterin-dependent reactions, which include the synthesis of catecholamines, serotonin, and nitric oxide, as well as tyrosine.
- 14. If phenylalanine hydroxylase is defective, the biosynthetic route to Tyr is blocked and Tyr must be obtained from the diet.
- **15.** Glucose + 2CO<sub>2</sub> + 2NH<sub>3</sub>  $\rightarrow$  2 aspartate + 2H<sup>+</sup> + 2H<sub>2</sub>O

- 1. Two hundred molecules of ATP are converted into AMP + 400  $P_i$  to activate the 200 amino acids, which is equivalent to 400 molecules of ATP. One molecule of GTP is required for initiation, and 398 molecules of GTP are needed to form 199 peptide bonds.
- **2.** The rate would fall because the elongation step requires that the GTP be hydrolyzed before any further elongation can take place.
- **3.** The nucleophile is the amino group of the aminoacyl-tRNA. This amino group attacks the carbonyl group of the ester of peptidyl-tRNA to form a tetrahedral intermediate, which eliminates the tRNA alcohol to form a new peptide bond.
- **4.** EF Ts catalyzes the exchange of GTP for GDP bound to EF Tu. In G-protein cascades, an activated 7TM receptor catalyzes GTP–GDP exchange in a G protein.
- 5. The  $\alpha$  subunits of G proteins are inhibited by a similar mechanism in cholera and whooping cough.
- **6.** Because the tRNA is going to be released from the E-site, codon recognition and pairing with the anticodon are in no way advantageous and may, in fact, be detrimental to smooth release.
- 7. If  $\delta$  is the probability that an error is committed at each step, then 1- $\delta$  is the probability

that an error has *not* been made in any one step. The probability that no error has been made in *any* of the *n* steps is then  $(1 - \delta)^n$ . This is the probability and the protein is entirely error-free.

- **8.** (*a*) 0.990.
  - (b) 0.904. In this case, nearly 10% of the proteins would contain one or more errors.
- **9.** No; because nearly all the amino acids have more than one codon (*e.g.*, Leu has six), any given polypeptide can be coded for by a number of different base sequences. However, because some amino acids are encoded by only one codon and those with multiple codons often share the same nucleotide at two of the three positions, *certain parts* of the mRNA sequence encoding a protein of known amino acid sequence can be predicted with high certainty.
- **10.** The amino acid most recently added to a growing polypeptide chain is the only one covalently attached to a tRNA and hence is the only link between the polypeptide and the mRNA that is encoding it. A proofreading activity would sever this link, halting synthesis of the polypeptide and releasing it from the mRNA.

## CHAPTER - 29

- 1. Multiple lysosomal enzymes are severely deficient in the lysosomes and are actually found in abnormally high levels in sera and other body fluids. Mannose 6-phosphate is the signal to target enzymes to lysosomes. The first step is addition of *N*-acetylglucosamine phosphate to high-mannose oligosaccharides. Subsequent cleavage, leaving the phosphate behind, produces the mannose 6-phosphate signal. Lack of lysosomal enzymes means that undegraded products accumulate in lysosomes– thus forming inclusion bodies.
- **2.** These structure are all targeting signals to send proteins to particular subcellular particles. The three indicated are targets for mitochondria, nucleus, and peroxisomes, respectively.

- 1. (a) 5'-UAACGGUACGAU-3'.
  - (**b**) Leu-Pro-Ser-Asp-Trp-Met.
  - (c) Poly(Leu-Leu-Thr-Tyr).
- 2. Only single-stranded RNA can serve as a template for protein synthesis.
- **3.** Incubation with RNA polymerase and only UTP, ATP, and CTP led to the synthesis of only poly(UAC). Only poly(GUA) was formed when GTP was used in place of CTP.
- **4.** These alternatives were distinguished by the results of studies of the sequence of amino acids in mutants. Suppose that the base C is mutated to C'. In a nonoverlapping code, only amino acid 1 will be changed. In a completely overlapping code, amino acids 1, 2 and 3 will all be altered by a mutation of C to C'. The results of amino acid sequence studies of tobacco mosaic virus mutants and abnormal hemoglobins showed that alterations usually affected only a single amino acid. Hence, it was concluded that the *genetic code is nonoverlapping*.
- 5. Highly abundant amino acid residues have the most codons (*e.g.*, Leu and Ser each have six), whereas the least-abundant amino acids have the fewest (Met and Trp each have only one). Degeneracy (*a*) allows variation in base composition and (*b*) decreases the likelihood that a substitution for a base will change the encoded amino acid. If the degeneracy were equally distributed, each of the 20 amino acids would have three codons. Both benefits

(*a* and *b*) are maximized by the assignment of more codons to prevalent amino acids than to less frequently used ones.

- 6. No. The the term "reading frame" refers to the number of bases contained in each codon. The reason that (+ + +) or (- -) restored the reading frame is because the code is triplet. By having the (+ + +) or (- -), the translation system is "out of phase" until the third "+" or "-" is encountered. If the code contained six nucleotides (a sextuplet code), then the translation system is "out of phase" until the sixth "+" or "-" is encountered.
- 7. Assume that you have introduced a copolymer (ACACACAC ...) to a cell-free protein synthesizing system. There are two possibilities for establishing the reading frames : ACA, if one starts at the first base and CAC if one starts at the second base. These would code for two different amino acids (ACA = threonine; CAC = histidine) and would produce repeating polypeptides which would alternate *Thr-His-Thr-His ... or His-Thr-Hi*

Because of a triplet code, a trinucleotide sequence will, once initiated, remain in the same reading frame and produce the same code all along the sequence regardless of the initiation site. Given the sequence CUACUACUA, notice the different reading frames producing three different sequences, each containing the same amino acid.

- 8. From the repeating polymer ACACA . . . one can say that threonine is either CAC or ACA. From the polymer CAACAA . . . with ACACA . . ., ACA is the only codon in common. Therefore, threonine would have the codon ACA.
- **9.** The basis of the technique is that if a trinucleotide contains bases (a codon) which are complementary to the anticodon of a charged tRNA, a relatively large complex is formed which contains the ribosome, the tRNA, and the trinucleotide. This complex is trapped in the filter whereas the components by themselves are not trapped. If the amino acid on a charged, trapped tRNA is radioactive, then the filter becomes radioactive.
- 10. (a) Starting from the 5' end and locating the AUG triplets, one finds two initiation sites leading to the following two sequences :

Met-His-Tyr-Glu-Thr-Leu-Gly

Met-Arg-Pro-Leu-Gly.

- (b) In the shorter of the two reading sequences (the one using the internal AUG triplet), a UGA triplet was introduced at the second codon. While not in the reading frames of the longer polypeptide (using the first AUG codon), the UGA triplet eliminates the product starting at the second initiation codon.
- **11.** The central dogma of molecular genetics and to some extent, all of biology, states that DNA produces, through transcription, RNA, which is "decoded" (during translation) to produce proteins.
- 12. RNA polymerase from *E. coli* is a complex, large (almost 500,000 daltons) molecule composed of subunits ( $\alpha$ ,  $\beta$ ,  $\beta'$ ,  $\sigma$ ) in the proportion  $\alpha 2$ ,  $\beta$ ,  $\beta'$ ,  $\sigma$  for the holoenzyme. The  $\beta$  subunit provides catalytic function while the sigma ( $\sigma$ ) subunit is involved in recognition of specific promoters. The core enzyme is the protein without the sigma.

Proline :	$C_3$ , and one of the $C_2A$ triplets	
Histidine :	one of the C <sub>2</sub> A triplets	
Threonine :	one C <sub>2</sub> A triplet, and one A <sub>2</sub> C triplet	
Glutamine :	one of the $A_2C$ triplets	
Asparagine :	one of the $A_2C$ triplets	
Lysine :	A <sub>3</sub>	
	Histidine : Threonine : Glutamine : Asparagine :	

- 14. A gene is responsible for the amino acid sequence of a protein, which may or may not be an enzyme or part of an enzyme. The gene also controls the amount of the protein synthesized at any one time.
- **15.** After synthesis, the product of RNA polymerase II, messenger RNA, is capped with 7-methylguanosine, a poly(A) tail is added, and introns are removed.
- Met–Pro–Gly–Asn–Thr–Ala–Gly–Asn–Ser Met–Pro–Gly–Lys–His–Ser–Arg–Glu
- 17. Overlapping codes affect two or more protein products during a mutational event, which may be more severe. Overlapping coding sequences allow compaction of information. More information can be stored in a shorter sequence.

- 1. Potential hydrogen-bond donors at pH 7 are the side chains of the following residues: arginine, asparagine, glutamine, histidine, lysine, serine, threonine, tryptophan, and tyrosine.
- **2.** A high blood-glucose level would trigger the secretion of insulin, which would stimulate the synthesis of glycogen and triacylglycerols. A high insulin level would impede the mobilization of fuel reserves during the marathon.
- **3.** Lipid mobilization can occur so rapidly that it exceeds the ability of the liver to oxidize the lipids or convert them into ketone bodies. The excess is reesterified and released into the blood as VLDL.
- **4.** A role of the liver is to provide glucose for other tissues. In the liver, glycolysis is used not for energy production but for biosynthetic purposes. Consequently, in the presence of glucagon, liver glycolysis stops so that the glucose can be released into the blood.
- **5.** The phosphodiesterase in photoreceptor cells is homologous to PDE5 and is inhibited to some extent by sildenafil, leading to visual side effects.
- 6. The end organ is adrenal cortex. If cortisol is increased in response to an injection of ACTH, the adrenal cortex is functioning properly. An intravenous infusion of CRH (corticotropic-releasing hormone) should be able to reach the anterior pituitary. If ACTH increases in response to this, the pituitary is functioning so the problem is probably with the hypothalamus. If ACTH does not increase in response to CRH, the anterior pituitary is not functioning.
- 7. There are two cyclooxygenases. COX1 is a constitutively expressed enzyme that catalyzes the synthesis of required prostaglandins, for example, protection of the stomach lining and blood coagulation processes. COX2, however, is induced as part of the inflammatory response. NSAIDs (nonsteroidal antiinflammatory drugs like aspirin) inhibit both COX1 and COX2, so stomach irritation is common. COX2 drugs inhibit production of only the inflammatory prostaglandins.
- 8.  $1\alpha$ , 25-dihydroxycholecalciferol (1,25 (OH)<sub>2</sub>D<sub>3</sub>) is the active form of vitamin D. Ultraviolet light acting on the skin converts 7-dehydrocholesterol to cholecalciferol. This compound must be hydroxylated in liver to 25-hydroxycholecalciferol and subsequently in kidney to yield the active  $1,25(OH)_2D_3$ .
- **9.** It is presumed that starch increases blood glucose levels less than simple sugars do. Thus, there is less stimulation of insulin secretion. Insulin would tend to retard energy mobilization from intracellular stores– something not desirable during a marathon.
- **10.** Liver contains low levels of the enzyme that synthesizes acetoacetyl-CoA from acetoacetate, ATP, and CoA-SH. Therefore, when liver synthesizes ketone bodies, they cannot readily

be activated for catabolism within the hepatocyte. Instead, they are released and ultimately utilized by other tissues.

11. (a) Heart and skeletal muscle lack the enzyme glucose-6- phosphate phosphatase. Any glucose-6-phosphate that is produced enters the glycolytic pathway, and under  $O_2$ -deficient conditions is converted into lactate *via* pyruvate.

(b) Phosphorylated intermediates cannot escape from the cell, because the membrane is not permeable to charged species. In a "fight or flight" situation, the concentration of glycolytic precursors needs to be high in preparation for muscular activity. The liver, on the other hand, must release the glucose necessary to maintain the blood glucose level. Glucose is formed from glucose-6-phosphate and passes from the liver cells to the bloodstream.

**12.** (*a*) Excessive utilization of blood glucose by the liver, leading to hypoglycemia; shutdown of amino acid and fatty acid catabolism

(b) Little circulating fuel is available for ATP requirements. Brain damage results because glucose is the main source of fuel for the brain.

- **13.** Thyroxine acts as an uncoupler of oxidative phosphorylation. Uncouplers lower the P/ O ratio, and the tissue must increase respiration to meet the normal ATP demands. Thermogenesis could also be due to the increased rate of ATP utilization by the thyroidstimulated tissue, because the increased ATP demands are met by increased oxidative phosphorylation and thus respiration.
- 14. Because prophormones and preprohormones are inactive, they can be stored in quantity in secretory granules. Rapid activation is achieved by enzymatic cleavage in response to an appropriate signal.
- 15. (a) estrogen.
- **16.** (*a*) Yes. Take it on an empty stomach and do not eat immediately afterward since food alters its absorption.
- **17.** (b) placenta.
- **18.** Peptide (or protein) hormones : Insulin and Growth hormone Steroid hormones : Testosterone and Estrogen
- **19.** Insulin and glucagon.
- 20. In diabetes mellitus, which is a disorder of the carbohydrate metabolism, glucose cannot enter the cells but remains concentrated in the blood instead. Thus, the cells starve in the midst of plenty. The increased amount of sugar in the blood also brings about adverse changes in the membrane transport system of the cells. The blood circulation is also impaired. A net result of all these changes is that opportunistic bacteria etc. flourish and skin infections especially at the extremities (toes etc) are common. Increased incidence of skin infection is only one of a group of complications that may set in due to diabetes. Skin is easily affected as it is the most easily accessible part of the body.
- **21.** Because of their low solubility in lipid, water-soluble hormones cannot penetrate the cell membrane; they bind to receptors on the outer surface of the cell. In the case of epinephrine, this receptor is an enzyme that catalyzes the formation of a second messenger (cAMP) *inside* the cell. In contrast, lipid-soluble hormones can readily penetrate the hydrophobic core of the cell membrane. Once inside the cell, they can act on their target molecules or receptors directly.
- **22.** (*a*) Aspirin
- **23.** (*a*) Neurotransmitter
- 24. (a) Pancreas
- **25.** A new study suggests that being obese during adulthood decreases lifespan by 3 years.

Obesity is defined as having a body mass index (BMI) of 30 or more. Obesity risks are similar to smoking risks

- 26. Iodine is an essential nutrient which is required in minute amounts for normal growth of animals and humans. Iodine deficiency results in impairment of the functioning of the thyroid gland, which produces 'thyroxine' hormone. *Since thyroxine controls the rate of body metabolism and growth, iodine deficiency leads to a variety of disorders like goitre in children or adults and impaired mental functioning, poor intellectual performance and muscular disorders in children.* Women with iodine deficiency give birth to stillborn babies. Iodization of salt offers the most convenient way of combating iodine deficiency. Firstly, because salt is an essential ingredient of our diet and secondly, one can never take too much of it. So by iodization of common salt, a minimum intake of iodine can be ensured for the entire population, thereby minimizing the incidence of iodine deficiency.
  27. (a) Thymus
- **28.** (*d*) Exophthalmic goitre
- **29.** (c) Calcitonin
- **30.** (*b*) Thyroxine

## **CHAPTER - 32**

- (a) Most plant hormones are terpenoid compounds.
   (b)There are no known peptide hormones in higher plants. Steroid-like compounds have been described in plants, but it is not clear that they act like steroid hormones.
- 2. Gibberellin and abscissic acid
- **3.** (c) cell enlargement

- 1. Water-soluble vitamins are more rapidly excreted in the urine and are not stored effectively. Fat-soluble vitamins have very low solubility in water and are excreted only very slowly by the kidney.
- 2. The proteins affected are those that have  $\gamma$ -carboxyglutamyl (Gla) residues, which are excellent calcium chelators. The formation of Gla is a posttranslational modification catalyzed by a carboxylase whose essential cofactor is vitamin K. Warfarin prevents the reduction of vitamin K epoxide formed during the carboxylation back to the dihydroquinone form, which is necessary for the reaction.
- 3. Vitamin K is necessary for carboxylation of specific glutamic acid residues in certain proteins to form  $\gamma$ -carboxyglutamic acid residues. In blood coagulation, this step is required for the conversion of preprothrombin to prothrombin. In bone formation, this is required to form the calcium-binding residues of the protein osteocalcin.
- 4. The usual recommended dose is 400 IU once a day.
- **5.** Despite what many people believe, vitamins pills or vitamin shots do not give you extra energy.
- **6.** No. If you take vitamin E while you are taking the anticlotting drug coumadin (warfarin), you could develop dangerous internal bleeding.
- 7. Yes, older people need extra vitamin D because they absorb less of it from their food and their skin makes less of it.
- 8. Ten to fifteen minutes of sunlight on the face and arms. Three times a week is usually

enough.

- **9.** (*b*) vitamin D
- **10.** (c) riboflavin
- **11.** The vitamins from the two sources are identical; the body cannot distinguish the source.
- 12. Ordinarily 400 I.U., but if one is over 50, 600 I.U. and if over 70, 800–1,000 I.U. a day
- **13.** No. 5,000 I.U. a day can cause permanent kidney damage, but taking up to 2,000 I.U. a day is usually safe.
- 14. (a) rhodopsin
- **15.** (*b*) calciferol (vitamin D)
- **16.** Yes, as one grows older, his skin makes less and less vitamin D and one needs to take more orally.
- **17.** After eating. This shows its movement through the intestive allowing more time for the pill to dissolve completely and be absorbed.
- **18.** No. These foods contain thousands of substances that have not been identified yet and that they fight cancer and other health problems.
- **19.** Not, if the vitamin pills contain iron. The iron can keep the thyroid pills from being adequately absorbed.
- **20.** (*b*) Spirulina

- 1. Glucose is the primary fuel of the brain, and the brain is particularly sensitive to any change in the availability of glucose for energy production. A key reaction in glucose catabolism is the thiamine pyrophosphate-dependent oxidative decarboxylation of pyruvate to acetyl-CoA, and thus a thiamine deficiency reduces the rate of glucose catabolism.
- 2. One of the reactions in which vitamin  $B_{12}$  participates is conversion of methylmalonyl CoA to succinyl CoA (a step in the catabolism of valine and isoleucine). Methylmalonyl CoA is a competitive inhibitor of malonyl CoA in fatty acid biosynthesis, necessary for the maintenance of the myelin sheath. Secondly, methylmalonyl CoA can be used in fatty acid synthesis leading to formation of branched-chain fatty acids, which might disrupt normal membrane structure.
- **3.** Five servings of fruits and vegetables a day will give one plenty of vitamin C (200 mg) ---- you would not need many supplements.
- 4. (d) choline
- 5. (a) nicotinic acid
- **6.** (*a*) folic acid
- 7. Yes,  $B_{12}$  is found only in animal products. To compensate, get  $B_{12}$  from a supplement or fortified products such as soy milk.
- **8.** (b) vitamin  $B_1$
- **9.** A new study showed that people with high homocysteine levels were twice as likely to develop Alzheimer's as those with low levels. To cut the risk of Alzheimer's, take a multivitamin that has B<sub>6</sub>, B<sub>12</sub> and folic acid. Wheat germ is a good source of B vitamins and folic acid.
- **10.** (*c*) vitamin  $B_{12}$
- 11. Possibly. Vitamin  $B_{12}$  and folate deficiencies may cause symptoms of depression and may

also cause a poor response to antidepressants.

12. Doctors prescribe vitamin tablets along with any antibiotic prescription to prevent our body from suffering vitamin deficiency. The antibiotics are powerful chemicals that can kill microorganisms, chiefly bacteria. When ingested these drugs kill not only the disease-causing bacteria but also the harmless ones normally residing in our intestines. Called the 'intestinal microflora', these friendly bacteria convert some of the food constituents into vitamin precursors which are absorbed into the body through intestine. But for this help some of the essential vitamins like those of vitamin-B complex will not be available for us, for our body lacks the machinery to convert food constituents into vitamin precursors. Use of powerful antibiotics kills these helpful bacteria and curtail the supply of vitamin precursors to the body. Therefore, in order to keep the body supplied with usual dose of vitamins, doctors prescribe readymade easily absorbable vitamin-B tablets along with antibiotics. Vitamins are also believed to help in early recovery from the ailments.

# **CHAPTER - 35**

- 1. A 1 mg/ml solution of myoglobin (17.8 kd) corresponds to  $5.62 \times 10^{-5}$  M. The absorbance of a 1-cm path length is 0.84, which corresponds to an  $I_0/I$  ratio of 6.96. Hence, 14.4% of the incident light is transmitted.
- 2. Tropomyosin is rod shaped, whereas hemoglobin is approximately spherical.
- **3.** 50 kd.
- **4.** (*a*) Gel chromatography or gel electrophoresis.

(b) Add proteins of known molecular weight and obtain a standard curve in which either volume of the effluent (for chromatography) or the distance migrated (for electrophoresis) is plotted against molecular weight.

- 5.  $(1.7 + 1.3)/2 = 1.5 \text{ g/cm}^3$ .
- 6. The molarity of the solution is (1/423) = 0.032. The molar extinction coefficient is 0.27/(0.032/423) = 3,569.
- 7. (b) radioactive carbon compounds
- 8. No. To move an object x units north and the y units east brings the object to the same place reached by moving it first y units east and then x units north.
- **9.** (*a*) No, since differences in shape can affect mobility, *i.e.*, two proteins differing in both molecular weight and shape might have the same electrophoretic mobility.
  - (**b**) Yes.