Assortment of dietary oils (liquids) and fats (solids). Oils have a lower melting point because they contain unsaturated fatty acids. These lower the level of cholesterol in the blood.

Essential fatty acids must be obtained in the diet

The body is able to synthesize the required saturated and mono-unsaturated fatty acids from other precursors, but is unable to make two polyunsaturated fatty acids, linoleic acid and linolenic acid. Their structures are as follows:

linoleic acid (omega-6-fatty acid)	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$
linolenic acid (omega-3-fatty acid)	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$

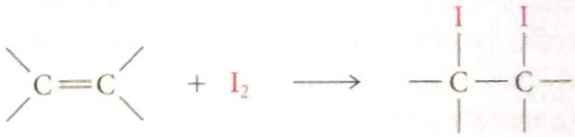
The terms omega-6 and omega-3 fatty acids refer to the position of the first double bond in the molecule relative to the terminal $-CH_3$ group. This is referred to as omega (the last letter in the Greek alphabet), to represent its distance from the $-COOH$ group. These structures (as condensed formulas) are given in Table 22 of the IB Data booklet.

Because they cannot be made in the body, these fatty acids must be obtained in the diet and are therefore known as **essential fatty acids**. They are obtained from plant and fish sources, for example, shellfish, leafy vegetables, canola oil and flaxseed oil. It has been shown that they play a part in many metabolic processes, including the synthesis of a group of lipids called prostaglandins which are involved in processes such as lowering blood pressure. As mentioned earlier in this section, there is also now evidence that these fatty acids, especially omega-3-fatty acids, play a role in lowering LDL cholesterol and hence help to protect against heart disease.

When linoleic and linolenic fatty acids were first discovered to be essential nutrients in 1923, they were originally designated as Vitamin F. Like vitamins, they give rise to deficiency disorders when absent from the diet. However, later work showed that they are better classified with the fats than with the vitamins.

Determination of the degree of unsaturation in a fat uses iodine

Unsaturated fatty acids are able to undergo **addition reactions**, by breaking the double bond and adding incoming groups to the new bonding positions created on the carbon atoms. (This is a characteristic reaction of alkenes, described in Chapter 10.) Iodine (I_2) is able to react with unsaturated fats in this way.



The iodine number of a fat is defined as the number of grams of iodine which reacts with 100 g of fat.

The equation shows that one mole of iodine will react with each mole of double bonds in the fat. Therefore the higher the number of double bonds per molecule, the larger the amount of iodine that can react. This is expressed as the **iodine number**, defined as the number of grams of iodine which reacts with 100 grams of fat. It is therefore a measure of the amount of unsaturation in the fat.

Determination of the iodine number of a fat usually involves reacting a known amount of the fat with a known amount of iodine and waiting for the reaction to be completed. The amount of excess iodine remaining can then be calculated by titration with $Na_2S_2O_3(aq)$ from which the reacted iodine can be determined.

Worked example

Linoleic acid has the formula $C_{18}H_{32}O_2$. Determine the iodine number of linoleic acid.

Solution

The formula for linoleic acid can be expressed as $C_{17}H_{31}COOH$, from which we can deduce that it has two carbon–carbon double bonds.

Therefore 2 moles I_2 will react with 1 mole linoleic acid.

M_r for linoleic acid = 280 g mol^{-1} and M_r for I_2 = 254 g mol^{-1}

Therefore 280 g linoleic acid reacts with 508 g I_2

So 100 g reacts with $\frac{508 \times 100}{280} = 181$ g

Therefore iodine number = 181

Exercise

5 A sample of fat containing 0.02 moles of fatty acid was found to react with 10.16 g of iodine. Determine the number of carbon–carbon double bonds present in the fatty acid.

Addition reactions to unsaturated fats are used in the food industry

You may have seen the term 'partially hydrogenated fat' on food labels. This refers to oils which have been chemically modified by addition reactions as described above, using hydrogen to add across double bonds and so decrease the degree of unsaturation. The outcome is a fat which, being more saturated, has a higher melting point and therefore is in a more convenient form for packing and storage as a solid or semi-solid. Fats made in this way also break down less easily under conditions of high temperature frying and usually have a longer shelf life than liquid oils. Most margarines and shortening come into this category.

Foods containing *trans* fats produced by hydrogenation. The process is used to solidify fats and extend their shelf life, but has been linked to increased risk of heart disease.

There is, however, a problem with this process. The chemical modifications involve heat and pressure treatments, during which a chemical change occurs affecting the positions of the groups around the remaining double bonds, altering them from the so-called *cis* position on the bond to the *trans* position. The resulting fats are therefore known as ***trans* fats**. They are particularly prevalent in processed foods and are always present when food is described as 'partially dehydrogenated'. Evidence shows that consuming *trans* fats raises the level of LDL cholesterol which is a risk factor for heart disease. Furthermore, *trans* fats reduce the blood levels of HDL cholesterol which protects against heart disease. So *trans* fats, like saturated fats and for the same reason, must clearly be reduced or eliminated from a healthy diet. Limiting the intake of commercially fried food and high fat bakery products is an important step in this process.

The growing awareness of the link between *trans* fats and heart disease has caused many different responses around the world. Denmark has the strictest *trans* fats legislation of all countries and since 2004 these fats have effectively been banned. Canada was the first country to introduce mandatory labelling of *trans* fats on food products and this had an effect on the food manufacturing industry, actively reducing the *trans* fat content of their food. In 2007 New York City banned restaurants from using them and other major American cities are likely to follow suit. The World Health Organization has recommended that all governments phase out use of *trans* fats if labelling alone does not spur significant reductions. The cost of this is, however, considerable as it will involve major changes in food formulations.

Digestion of fats

Fats and oils are insoluble molecules so cannot be transported in the blood. They are therefore broken down to their component molecules (fatty acids and glycerol) in the gut in the process of digestion. This involves hydrolysis reactions, in which water is used, under the control of enzymes known as **lipases**.

Lipases are secreted in different parts of the gut and act sequentially to complete the digestion of the lipid as it passes through. Typically these are the slowest molecules to be broken down in digestion and may take many hours before they are made soluble and can be absorbed into the blood. Lipases, being enzymes and hence made of protein, are very sensitive to changes in the pH of the medium. Controlling the pH in different parts of the gut is therefore one way in which the body controls lipid digestion.

2 Structure of phospholipids

Phospholipids are similar to triglycerides in that they are also derived from fatty acids and glycerol, but have only two fatty acids condensed onto the glycerol molecule. The third —OH position of the glycerol has, instead, condensed with a phosphate group. Different phospholipids vary in their fatty acid chains and in the group attached to the phosphate. One of the most common phospholipids is known as **lecithin** shown below.

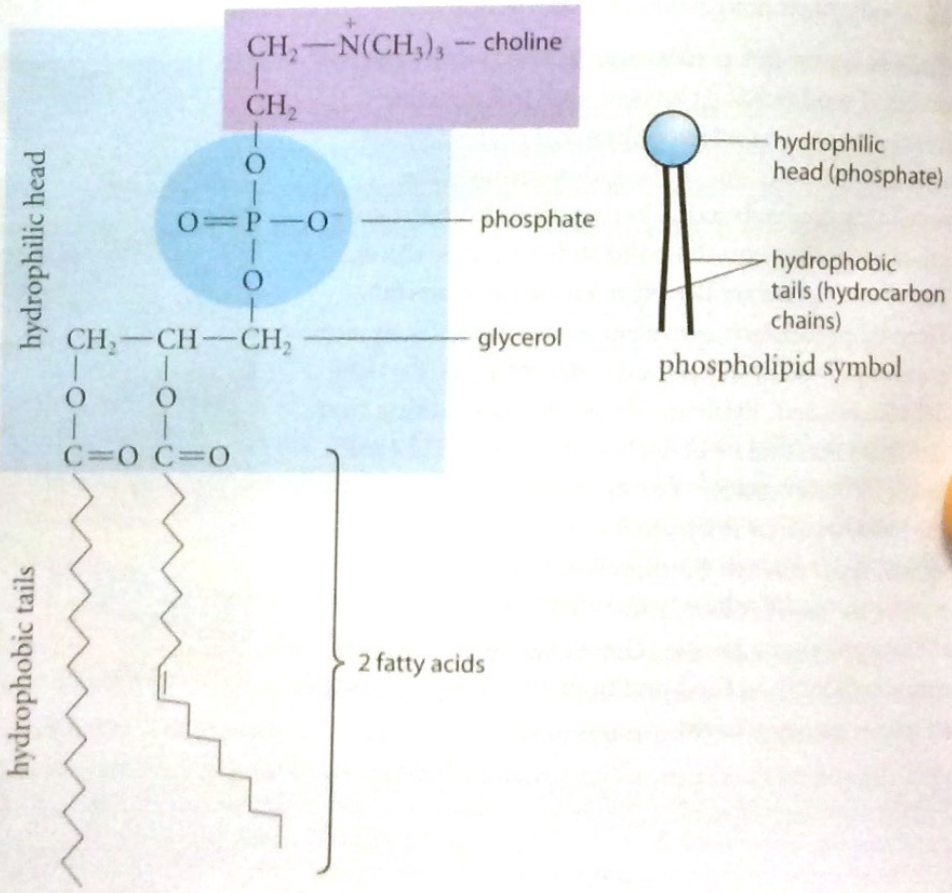


Figure 13.23 Representations of the structure of phospholipids.

Phospholipids are characterized by having a polar, or hydrophilic 'head' (the phosphate group) and two non-polar, or hydrophobic 'tails' (the hydrocarbon chains of the fatty acids). As a result they will spontaneously form a **phospholipid bilayer** which maximizes the interactions between the polar groups and water, while creating a non-polar (hydrophobic) interior.

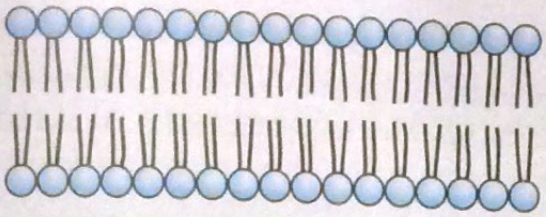
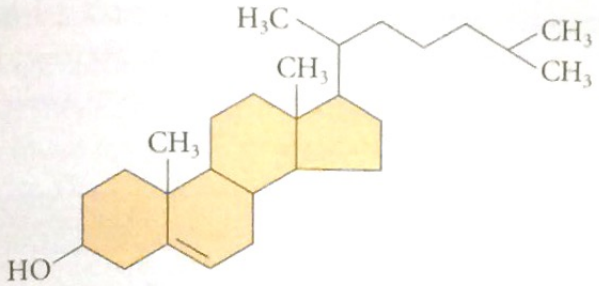


Figure 13.24 Phospholipid bilayer.

This phospholipid bilayer provides the basis of membrane structure.

3 Structure of steroids

Steroids are lipids with a structure consisting of four fused rings. One of the most important steroids is **cholesterol** which has the following structure.



cholesterol

Figure 13.25 Structure of cholesterol.

Cholesterol is the steroid used in the body in the synthesis of many other steroids, including the sex hormones. The uses and problems of cholesterol in the body were discussed earlier in this section.

W You can read a summary and test yourself on the biochemistry you have learned so far. There are links from here to other sites.

Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

B.5 Micronutrients and macronutrients

Nutrients are classified according to amounts needed

The term 'nutrients' refers to molecules that are required in the diet for absorption and use by the body. Given the complexity of metabolic processes, it is not surprising that we need an equally complex array of nutrients to maintain health. A key concept in the consideration of a healthy diet is *balance* between the different types of nutrients. It is convenient to classify nutrients roughly according to the amounts in which they are needed, usually expressed as the **recommended daily intake**.

Micronutrients are those needed in extremely small amounts, generally less than 0.005% of body mass. Their quantities are so small they are usually measured in mg or μg per day. These substances are needed to enable the body to produce enzymes, hormones and other substances essential for health. As tiny as the amounts are, however, the consequences of their absence are severe. Micronutrients include the **vitamins** and many so-called **trace minerals** such as Fe, Cu, Zn, I, Se, Mn, Mo, Cr, Co and B.

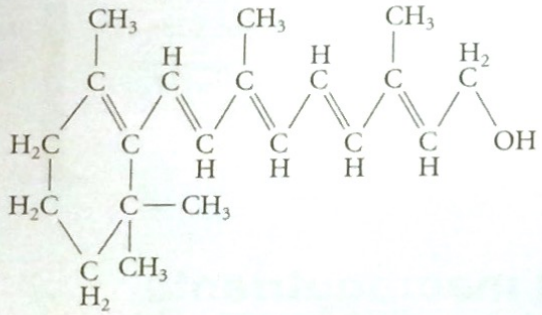
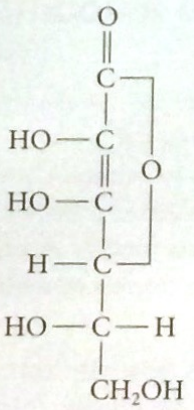
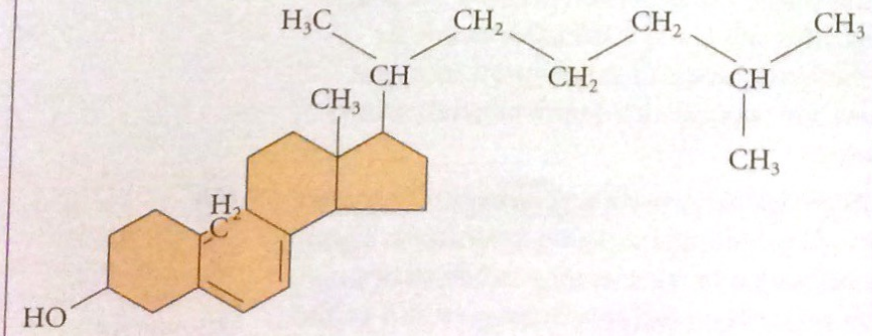
Macronutrients are those nutrients needed in relatively large amounts. They are used to provide energy in the body and to build and maintain its structure. They include the macromolecules described earlier in this chapter – carbohydrates, proteins and lipids – as well as some minerals needed on a larger scale such as Na, Mg, K, Ca, P, S and Cl.

i The average adult has 1.0–1.5 kg of calcium in their body, of which 99% is found in bones and teeth; the remainder is in body fluids and membranes.

Vitamins are organic micronutrients

Vitamins are organic compounds, needed in small amounts for normal growth and metabolism, which are not synthesized in the body. They are usually broken down by the reactions in which they are involved, so must be taken in the diet.

Vitamins vary in whether they are principally soluble in water or in fat. Water-soluble vitamins are transported directly in the blood and excesses are filtered out by the kidneys and excreted. Fat-soluble vitamins are slower to be absorbed and excesses tend to be stored in fat tissues where they can produce serious side-effects. Differences in their structure determine these solubility differences. Vitamins that are water soluble have polar bonds and the ability to form hydrogen bonds with water. Those that are fat soluble are mostly non-polar molecules with long hydrocarbon chains or rings. The structures of some important vitamins are given in Table 21 of the IB Data booklet, so they do not have to be learned. It is important, though, that you can explain their different solubilities through interpreting their structures.

Vitamin	Structure	Solubility and properties
A retinol		Fat soluble Hydrocarbon chain and ring are non-polar and influence the solubility more than the one —OH group. Involved in the visual cycle in the eye and particularly important for vision at low light intensity.
C ascorbic acid		Water soluble Several —OH groups enable hydrogen bonds to form with water. Acts as cofactor in some enzymic reactions and important in tissue regeneration following injury and also helps give resistance to some diseases.
D calciferol		Fat soluble Predominantly a hydrocarbon molecule with four non-polar rings and only one —OH group. Note its chemical similarity to cholesterol. Stimulates the uptake of calcium ions by cells and so is important in the health of bones and teeth.

Vitamin C contains several functional groups (—OH and —C=C—) that are relatively easily oxidized. This is why the vitamin is easily destroyed by most methods of food processing and storage and is hence best obtained from *fresh* fruits and vegetables.

The lack of vitamin C in stored foods was the reason many sailors on long voyages suffered from a deficiency disease known as scurvy in the 1800s. The symptoms of this are bleeding gums, poor resistance to infection and dark spots on the skin; if untreated it is fatal. Because the concept of a disease resulting from the *lack* of a dietary component was not understood, it took a long time to establish the link between scurvy and vitamin C deficiency. Meanwhile, the British Navy found that supplementing the diet of the crew with limes prevented occurrence of the disease, which is why British people are sometimes still known as 'limeys' in America.

Exercise

6 By referring to Table 21 in the IB Data booklet, identify one vitamin that is water soluble and one vitamin that is fat soluble. Explain the differences in solubility in terms of their structures and intermolecular forces.

Malnutrition is the result of deficiencies or imbalance in the diet

When people do not obtain a regular, balanced supply of the diverse nutrients needed in the diet, they suffer from **malnutrition**. This describes a broad spectrum of conditions that are always associated with compromised health and increased mortality. The main focus of malnutrition has traditionally been the large variety of nutrient-deficiency diseases and in particular the incidence of these in underdeveloped countries. But malnutrition is not uniquely the concern of poor countries. Increasingly the world is seeing a dramatic increase in diseases caused by high consumption of processed, energy-dense but micronutrient-poor foods. The term *malnutrition* can therefore also be used to describe the resulting chronic diseases such as obesity and diabetes particularly prevalent in industrialized countries.

Micronutrient deficiencies

The World Health Organization has identified iodine, vitamin A and iron deficiencies as the most important micronutrient deficiencies in global health terms, so these three will be discussed here.

'Freedom from hunger and malnutrition is a basic human right and their alleviation is a fundamental prerequisite for human and national development.' World Health Organization

Iodine is needed in the diet for the synthesis of the hormone thyroxine, which regulates the metabolic rate. It is present in most types of seafood and in some vegetables. A lack of iodine in the diet causes a swelling of the thyroid gland in the neck, known as **goitre**. In children, iodine deficiency is considered to be the world's largest cause of preventable mental retardation. The main strategy for the control of iodine deficiency is through adding it to salt, which has an extremely low cost.

Despite its extraordinary progress in reducing the rate of iodine deficiency in most parts of the world, the salt iodization programme has been much less successful in many parts of Europe. In addition, there is growing evidence that iodine deficiency is reappearing in some European countries where it was thought to have been eliminated. The reasons for these trends are currently the subject of research and policy review.

Bangladeshi woman with large goitre. This swelling of the neck is caused by enlargement of the thyroid gland owing to lack of iodine in the diet. Treatment includes an iodine-rich diet of fish and iodized salt.

Vitamin A (retinol) is needed in the diet for healthy skin (acne treatment), good eyesight and protection against some damaging effects of toxins, as it is an antioxidant. It is found in orange and yellow fruits and vegetables, spinach and egg yolks. A deficiency in vitamin A causes **xerophthalmia**, a condition characterized by dry eyes and also night blindness. Since it is a fat-soluble vitamin it has been found that it can be effectively added to margarine in a process known as 'vitamin A fortification'. The process is simple and inexpensive and has been found to reduce levels of xerophthalmia in many parts of the world. The potential of rice as a vehicle for vitamin A fortification is also being explored, given that rice is an important staple in many countries where the prevalence of vitamin A deficiency is high.

Child suffering from rickets. Rickets is a disease in growing children in which the bones do not harden and are malformed owing to a deficiency in vitamin D which is necessary for the uptake of calcium.

Iron deficiency is currently considered to be the most prevalent micronutrient deficiency in the world. Because iron is an essential part of haemoglobin, which is the pigment in red blood cells responsible for transporting oxygen around the body, its deficiency leads to a serious condition known as **anaemia**. The symptoms of this are fatigue, brittle nails, poor endurance and lowered immunity. Iron is found in red meats, green leafy vegetables, nuts and seeds. While its dietary deficiency is a cause of concern in many parts of the world, the question of how best to alleviate this is complicated by the fact that iron supplementation may increase the susceptibility to malaria, which is also widespread. Iron fortification has been found to be most effective when added with vitamin C to cereal flours and milk products.

Some other significant micronutrient deficiencies and their resulting diseases are summarized in the table below.

Micronutrient	Deficiency condition or disease
niacin, vitamin B3	pellagra: dermatitis, diarrhoea and dementia
thiamin, vitamin B1	beriberi: weight loss, fatigue and swelling
ascorbic acid, vitamin C	scurvy: bleeding gums, lowered resistance to infection and dark spots on the skin
calciferol, vitamin D	rickets: softened and deformed bones
selenium	Kashin–Beck disease: atrophy and degeneration of cartilage. This occurs particularly in parts of northern Russia and China where the soil is Se deficient.

Exposure to sunlight is an important source of vitamin D as ultraviolet rays trigger its synthesis in the skin. But increasingly it is becoming known that ultraviolet light also has a damaging effect on the skin and can be the cause of skin cancers (Chapter 16), which necessitates the use of sunscreens. Sunscreens with a protection factor of 8 or greater will block UV rays that produce vitamin D. This makes it even more important to include good sources of vitamin D in the diet when sun exposure is limited in this way.

Macronutrient deficiencies

Severe malnutrition can include protein deficiency and when this is prolonged it is life threatening. Half of the 10.4 million deaths occurring in children younger than five years old in developing countries are associated with protein deficiencies.

Marasmus is a condition resulting from protein deficiency found mainly in infants from developing countries at the time of weaning or when a mother's milk is greatly reduced. It is characterized by failure to gain weight, followed by weight loss and emaciation. **Kwashiorkor** is a similar condition that affects young children whose diet is high in starch and low in protein.

Summary

In summary, we can see that the causes of malnutrition are varied and widespread. They include:

- lack of distribution of global resources
- depletion of nutrients in the soil and water cultures through soil erosion
- lack of education about, or understanding of, the importance of a balanced diet
- over-processing of food for transport and storage
- the use of chemical treatments such as herbicides in food production.

Equally, there are many possible solutions to the varying challenges of malnutrition. These include:

- fortification of different staple foods with micronutrients
- the availability of nutritional supplements in many forms
- possible improvements in nutrient content of food through genetic modification
- increased labelling of foods with content information
- education regarding the nature of a balanced diet and promotion of the importance of personal responsibility in dietary choices.

As we reach the end of this section on the chemistry of the molecules in your diet and how they affect your health, you may like to ask yourself in the light of what you have learned here, what changes to your diet do you think would be beneficial to your health? And how could you make those changes?

W You can visit the World Health Organization website to find out more about particular diseases of malnutrition by country. You can even view it in your own language. Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

B.6 Hormones

Different parts of the body are specialized to perform particular functions, but must communicate with each other to ensure the health of the whole. There are two main methods of communication in the body: the nervous system, which uses electrochemical messages and the endocrine system, which is based on chemical messengers known as **hormones**. The latter is the system we will discuss here.

Hormones have a variety of chemical structures, including many of the types of molecules described earlier in this chapter. Some are proteins, others are steroids, and still others are modified amino acids or fatty acids. What they have in common is the fact that they are produced in glands known as **endocrine glands**, which have no duct and so secrete the hormone directly into the blood. Once in the bloodstream, the hormones circulate throughout the body but bring about responses only in cells that have receptors for them, known as **target cells**. It is a little bit like communicating by sending a radio message – the waves are transmitted everywhere, but only working radios tuned to the appropriate frequency will detect them.

The position of some important endocrine glands in the body is shown in Figure 13.26.

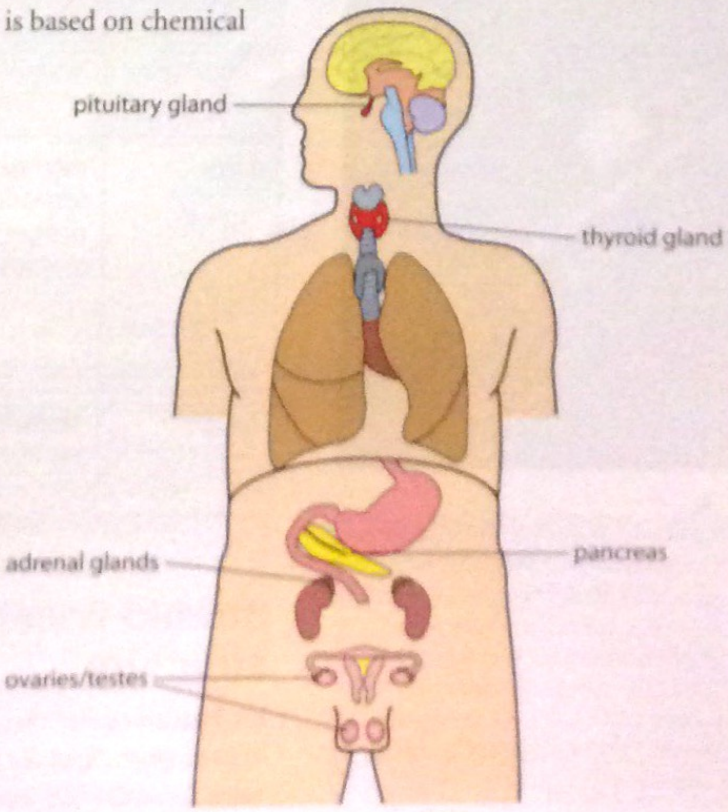



Figure 13.26 The human endocrine system